THE STRUCTURAL AND REACTION CHEMISTRIES OF SOME PLATINUM METAL COMPLEXES

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by

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DEDICATION

This thesis is dedicated to my

parents, Mrs N. T. Coll, and Mr K. P. Coll

and to the memory of the late Louise Mary Coll.

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ABSTRACT

The work described in this thesis is concerned principally with the preparation, photochemistry, and structural chemistry of some platinum metal complexes. The work is in two parts. The first part is a study of the photochemistry of complexes of the stoichiometric type $M(NO)X_nL_2$ n = 2 or 3 for M = Ru, Rh, Os, Ir; X = Cl, Br, I; and L = R_2S, R_2Se, Ph_3P, Ph_3As, and Ph_3Sb, and the second part is on the preparative and structural chemistries of halogeno- complexes of iridium, ruthenium and rhodium.

The main photochemical reaction observed was oxidation of the ligand (R_2S and R_2Se to R_2SO and R_2SeO, and R_3E to R_3EO for E = P, As, Sb), and in many instances the oxidised ligand subsequently coordinated to the complex. The oxidation is achieved with nitrogen oxides (NO, NO_2) for the organosulphides, organoselenides, triphenylphosphine and triphenylarsine, whereas for the triphenylstibine, O_2 appears to be the oxidisng agent. The photochemical reactions of the nitrosyl complexes were investigated using ^1H n.m.r., infrared, UV-visible and mass spectrometric methods.

The X-ray single crystal structures were determined on some starting materials and on some crystalline materials isolated during preparations of the complexes investigated in this work. The structures determined were; $RhCl_3(Et_2S)_2(Et_2SO)$, space group P1, a = 9.372(4) Å, b = 9.608(5) Å, c = 12.449(6) Å, α = 79.52(4)°, β = 86.88(3), γ = 70.66(3)°; $Os(NO)Br_3(Et_2S)(Et_2SO)$ space group $P2_1/c$, a = 13.398(3) Å, b= 8.501(2) Å, c = 16.199(3) Å, β = 105.69(1)°; $Ru(NO)Br_3(Et_2PPh)_2$ space group $P2_1/c$, a = 13.505(2) Å, b = 7.389(0) Å, c = 24.492(3) Å, β = 91.22(1), and $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$

space group $P2_1/c$; a = 10.869(1) Å, b = 11.381(1) Å, c = 22.673(2) Å β = 102.17(1)°.

During the preparative study of some trihalogenostannato-complexes of the type $A_3[MCl_n(SnX_3)_{6-n}]$ M = Rh, Ir; n = 1-3, a number of halogeno- complexes were produced. The X-ray single crystal structures of $K_3[IrCl_6]$ space group $P2_1/c$; a = 12.500(7) Å, b = 7.424(6) Å, c = 11.831(10) Å, β = 108.48(6)°, $(H_3O)_2[IrBr_6]$ space group Fm3m; a = 10.2738(28) Å, $(NH_4)_2[IrBr_6]$ space group Fm3m, a = 10.440(2) Å, $A_3[IrCl_5(SnCl_3)]$ for A = K space group $Pmn2_1$; a = 9.5873(13) Å, b = 9.5170(15) Å, c = 7.8480(9) Å, and A = NH_4 space group $Pmn2_1$; a = 9.593(3) Å, b = 9.495(2) Å, c = 7.832(2) Å, were determined.

A review of the preparative and X-ray structural studies of the platinum metal halogeno- complexes Ru, Os, Rh, Ir, has been prepared, covering the period from 1967 to 1987.

CHAPTER 1

INTRODUCTION

1.1 A SUMMARY OF THE PRESENT WORK

In this thesis two main subject areas were studied. In the first part the preparation and photochemical reactions of complexes of the type $M(NO)X_nL_2$ M = Ru, Os, Rh, Ir; X = Cl, Br, I; L= R_2S, R_2Se, or R_3E E = P, As, Sb, were investigated and in the second part the preparative and X-ray structural chemistries of some platinum metal halogeno- complexes were studied.

Chapter 2 contains a description of the nature of the metal-ligand bond for NO, organosulphides and organophosphines.

Page (1978) and Teow Sian Keong (1981) studied the photochemical reaction of the complex $Ru(NO)Br_3(Et_2S)_2$. They discovered that the reaction probably proceeded in two main steps; firstly forming a nitrosyl diethylsulphide diethylsulphoxide complex $Ru(NO)Br_3(Et_2S)(Et_2SO)$ followed by a dimeric complex $[Ru(NO)Br_3(Et_2SO)]_2$. Work is presented in Chapter 3 of a more detailed investigation of the reaction, and three possible mechanisms for the formation of the complex $Ru(NO)Br_3(Et_2S)(Et_2SO)$ are proposed. In addition a mechanism for the formation of the dimeric complex $[Ru(NO)Br_3(Et_2SO)]_2$ is given. Mass spectrometric studies suggest that the oxidising agent is NO_2, and that NO, initially coordinated to the metal, is a catalyst in the process. The photochemistry of organoselenide complexes of the type $Ru(NO)X_3(RR'Se)_2$ X = Cl, Br; R = Et, R' = Et, Ph was also studied. For the ethylphenylselenide compounds a complex mixture of products was produced, but for the

diethylselenide compounds it appears that the main product is a complex of the type $Ru(NO)X_3(Et_2Se)(Et_2SeO)$ which contains a coordinated diethylselenoxide ligand.

In Chapter 4 the preparative and photochemistries of the triphenylphosphine complexes $M(NO)X_3(PPh_3)_2$, for M = Os, Ru; X = Cl, Br, I are described. Mass spectrometric studies suggest that the oxidising agent in this case was NO. The main reaction products appear to be complexes of the type $M(NO)X_3(PPh_3)(OPPh_3)$ containing a coordinated triphenylphosphineoxide ligand. Diethylphenylphosphine complexes $Ru(NO)X_3(Et_2PPh)_2$ for X = Cl, Br, I were prepared and studied. The complexes exist in the trans configuration, but become cis meridional upon irradiation. The stereochemistry of the starting material $Ru(NO)Br_3(Et_2PPh)_2$ was determined by single crystal X-ray diffraction.

The photochemistry of rhodium and iridium triphenylphosphine complexes of the type $M(NO)X_2(PPh_3)_2$ is described in Chapter 5. In contrast to the Os and Ru triphenylphosphine complexes, all the NO is lost upon irradiation. The spectral evidence suggests that the resulting complexes contain coordinated $OPPh_3$, but pure products could not be isolated. There was also evidence for the formation of uncoordinated $OPPh_3$ in some cases. Attempts to prepare rhodium complexes of the type $Rh(NO)X_n(R_2S)_2$ were unsuccessful. However, the complex $RhCl_3(Et_2S)_2(Et_2SO)$ was isolated and studies of the preparation indicate that the oxidation of the Et_2S is achieved by NO liberated from the '$Rh(NO)Cl_n$' entity which is formed during the preparation. The single crystal X-ray structure was determined for $RhCl_3(Et_2S)_2(Et_2SO)$ and is described in Chapter 7. The crystals were

found to contain two different molecules in the asymmetric unit, each containing one sulphur bonded diethylsulphoxide ligand.

In Chapter 6 the photochemistry of some triphenylarsine complexes of the form $Ru(NO)X_3(AsPh_3)_2$ and $Rh(NO)X_2(AsPh_3)_2$ is described. Evidence was found for coordinated triphenylarsineoxide.

A summary of the findings of the photochemical reactions for the platinum metal complexes is given at the end of Chapter 6, and the effect of the halogeno- substituents and the platinum metal in the complex are discussed.

During attempts to prepare osmium diethylsulphide complexes, the complexes $Os(NO)X_3(Et_2S)(Et_2SO)$ for X = Cl, Br were obtained and the single crystal X-ray structure for $Os(NO)Br_3(Et_2S)(Et_2SO)$ was determined and is given in Chapter 7. The complex is isostructural with the Ru complex whose structure is known.

The complex $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$ was isolated during attempts to prepare $Os(NO)Cl_3(Et_2PPh)_2$ and the single crystal X-ray structure was determined for $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$ and is described in Chapter 7.

A microprocessor controlled mass spectrometer (SMS DATA QUAD) was used for analysis of the gaseous reaction products. Unfortunately part way through the study the instrument was damaged by other operators and was not able to be used for analysis of gaseous products in the latter part of the work. No other suitable mass spectrometer was available for the duration of the study.

A summary of the elemental analytical results and spectroscopic data is given at the end of each chapter. Because of the high formula weights for many of the complexes, there is little difference in the calculated elemental percentages for the complexes containing

unoxidised and oxidised ligands. Nonetheless the results are consistent with the suggested products and do serve as a good indication of the correctness of the stoichiometry. Literature surveys relevant to the work covered in the above chapters are given in the introduction to the chapter.

In Chapter 8 a review of the preparative and X-ray structural studies for the four platinum metals; Ru, Rh, Os, Ir is given. The scope of the review is outlined in Section 8.1, and the references for the review are given at the end of Chapter 8. Many of the references were published in Russian journals. English translations were obtained for most of these references, and the page numbers (in brackets) for the Russian originals are also given.

The preparative and structural chemistries of some hexahalogenometallate complexes and complexes containing trichlorostannato- ligands are described in Chapters 9 and 10. The single crystal X-ray structures are reported for $(NH_4)_2[IrBr_6]$, $(H_3O)_2[IrBr_6]$, $K_3[IrCl_6]$, and $K_3[IrCl_5(SnCl_3)]$. The structural relationships between $(NH_4)_3[IrCl_6]$ and $K_3[MCl_6]$, for M = Ir, Rh, Ru were investigated using X-ray powder diffraction and precession photography.

The physical methods employed during the work are described in Chapter 11.

CHAPTER 2

A DISCUSSION OF THE BONDING IN THE METAL-LIGANDS SYSTEMS STUDIED IN THIS THESIS

2.1 INTRODUCTION

The purpose of this chapter is to discuss some of the more important aspects of the transition metal to ligand bonding for the ligands used in this thesis. In addition some explanation will be given for the spectral properties and reactivity exhibited by the ligands and complexes.

Nitric oxide is an important ligand in the chemistry of transition metals and especially for ruthenium which forms a large number of complexes with nitric oxide [Griffith 1967; Seddon & Seddon 1984]. The nature of the metal-nitric oxide bond has been of considerable interest from quite early times [Green 1966; Moeller 1946a; Griffith 1966; Moeller 1946b] and it is only after study of the complexes using single crystal X-ray diffraction that the nature of this bond has been clearly established. Originally only one mode of bonding was considered viz. a linear M-N-O system with the formation of a σ-bond from overlap of the lone pair of electrons on the nitrogen atom with a metal orbital. This lone pair could be in either a p orbital or a sp hybrid orbital. However, observations from the infrared spectra of complexes had established that nitric oxide, relative to similar ligands such as carbon monoxide, exhibited an unusually wide range of values for its characteristic strong ν(NO) absorbance [Lewis et al. 1958; Moeller 1946a]. This prompted the suggestion that NO could bind to the central metal atom in one of two

different modes viz. linear and bent. This suggestion was confirmed when in 1968 the X-ray structural determination of the iridium complex $[IrCl(CO)(NO)(PPh_3)_2][BF_4]$ was carried out and found to contain a bent Ir-N-O system [Hodgson & Ibers 1968].

2.2 NITRIC OXIDE

2.2.1 Bonding in Free Nitric Oxide

In order to understand the way in which nitric oxide might coordinate to a metal centre it is important to consider the bonding within nitric oxide itself. The bonding in nitric oxide can be described, using a valence bond approach, as consisting of several different resonance forms. However, this approach is rather limited, and the observed bond order of 2.5 for nitric oxide is best explained by the molecular orbital approach. In the molecular orbital approach nitric oxide, a heteronuclear diatomic, is considered to have three filled bonding molecular orbitals, one σ and two π orbitals, and one half filled π^* antibonding orbital [Mahan 1969]. The molecular orbital diagram for nitric oxide is shown in Figure 2.1

2.2.2 Nitric Oxide as a Ligand

Nitric oxide may bind to a transition metal centre in a linear or a bent fashion. The two modes of coordination are illustrated in Figure 2.2. The molecular orbital description of the linear nitric oxide to metal bond involves the formation of two bonds i.e. σ and π components.

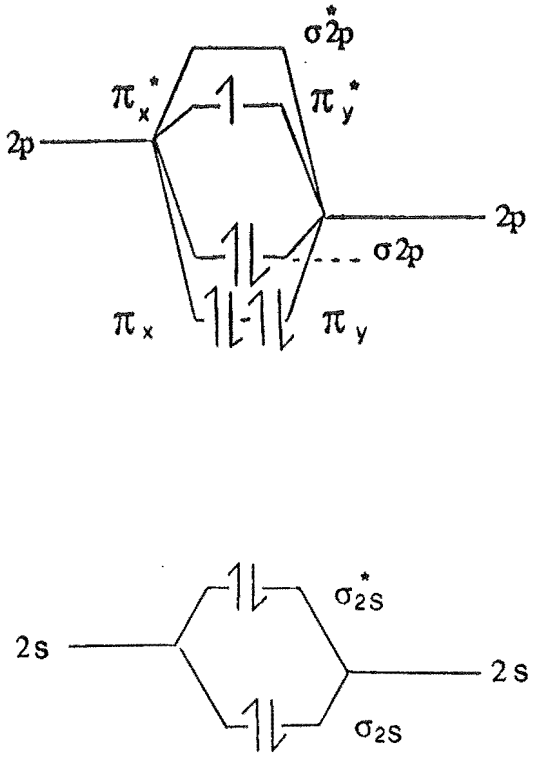
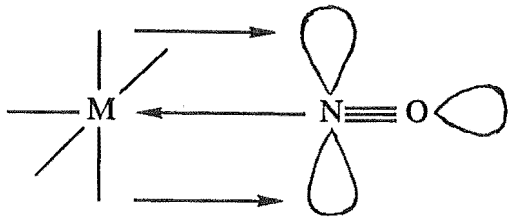


FIGURE 2.1

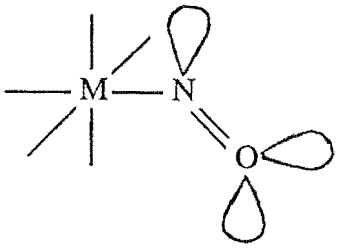
Molecular orbital diagram for nitric oxide

A σ bond is formed from the overlap of a filled nitrogen p orbital (or an sp hybrid) and a vacant d orbital of the transition metal. A metal to ligand π-back-bond is formed from a filled metal d orbital overlapping with a vacant antibonding orbital of the nitric oxide system. This approach assumes the NO group has lost an electron and is bound as NO^+. The wide range in the ν(NO) frequency is said to be related to the extent of this π-back-bonding. The extent of the π-back-bonding will be influenced by factors such as the other ligands present, the transition metal, and its oxidation state.



back bond

NO^+ Linear Coordination



NO^- Bent Coordination

FIGURE 2.2

Modes of coordination of nitric oxide to transition metals

For the bent mode of coordination the nitrogen atom is considered to use a filled sp^2 hybrid orbital to overlap with the vacant metal d orbital. In this case the NO is assumed to have gained an electron filling the half empty sp^2 hybrid orbital and thus is bound as NO^-. With this type of coordination the M-N-O bond angle is expected to be close to 120^o.

It was originally thought that the position of the ν(NO) in the infrared spectrum would be a guide to the mode of bonding. The linear binding mode was expected to produce a higher energy NO vibration due to the loss of an electron to form the NO^+ entity which increases the

NO bond to 3. In the bent mode the NO^- entity would have a bond order of 2. There are however many examples in which the linear coordinated NO group has a lower value for ν(NO) than the bent coordinated NO group [Mingos & Ibers 1971a; Pierpont et al. 1971]. The bonding of nitric oxide in a linear fashion explained as loss of the antibonding electron to give NO^+ followed by an electron transfer from NO to the metal and then the formation of a π-type back-bond from the metal back into the orbital from which the electron was originally removed, seems unnecessarily complicated. A simpler view is that of a metal to nitrogen σ-bond and a π-back-bond by donation of electron density from the metal centre into the partially filled antibonding orbital [Enenmark & Feltham 1974]. The extent of this back-bond transfer of electrons would be influenced by the other ligands present and especially by the π-acceptor ability of the ligand opposite the NO. Such a ligand will compete directly for the electron density available from the metal centre. Variation in the π-acceptor ability of competing ligands will therefore influence the M-NO back-bonding and the electron density in the NO antibonding orbital. This variation in the electron density in the antibonding orbital would explain the range in the ν(NO) infrared stretching frequencies.

The oxidation state of the metal also influences the electron density that is dispersed over a complex. If for example the metal is in a low oxidation state, then there is more electron density on the metal centre which may be dispersed into the NO antibonding orbital resulting in a lower value for the frequency of the ν(NO) absorbance. This means that even with similar ligands present in two complexes, variations can arise in the amount of electron density in the antibonding orbital of the NO system and explains why low values of

ν(NO) may be observed when the NO group is bound in the linear mode. Metal to ligand π-back-bonding is considered to be an important factor in stabilising metal ions when they are in low oxidation states [Chatt & Williams 1951; Nyholm & Tobe 1963]. There is considerable evidence that NO is a good π-acceptor [Snyder & Weaver 1970; Holsboer et al. 1973; Schultz et al. 1974] but a relatively poor σ-donor. Consequently NO tends to bind opposite ligands that are good σ-donors and poor π-acceptors, such as chlorine or oxygen. This is observed in structures with chlorine and NO, in which both the chlorine to metal and nitrogen to metal bond distances are shortened [Fergusson & Rodley 1975].

The mode of bonding as NO^+ or NO^- aids in the assignment of the metal oxidation state. Mostly this gives satisfactory results in terms of chemically reasonable oxidation states. However, there are some compounds where this is not the case [Cotton & Wilkinson 1972]. For example in the nitroprusside complex ion $[Fe(NO)(CN)_5]^{2+}$ this concept would suggest an oxidation state for the iron of +2. This is not supported by either the Mossbauer spectroscopic results or the chemical behaviour of the complex [Brown 1971]. The chemical shift value for the Mossbauer spectra whilst not clearly favouring either the +2 or +3 oxidation state for the iron atom, is closer to that of +3.

2.2.3 Reactivity of the Coordinated Nitric Oxide Ligand

The electron density on the nitrogen atom in coordinated nitric oxide has an influence on the reactivity of the ligand. Variation in this electron density may lead to the nitric oxide ligand exhibiting

reactivity towards both electrophilic and nucleophilic reagents. It has been suggested that linearly coordinated nitric oxide with a lower electron density on the nitrogen atom (i.e. where little π-back-bonding occurs) are susceptible to attack by nucleophiles, whilst bent coordinated nitric oxide with a higher electron density on the nitrogen atom is susceptible to attack from electrophiles [Eisenberg & Meyer 1975]. Reactivity of the coordinated nitric oxide to electrophiles and nucleophiles has been observed, and was at first a novel feature of a species that was traditionally inert to attack [Masek 1969; Bottomley et al. 1973; Addison & Lewis 1955].

Attempts have been made to relate this reactivity to the mode of coordination [Bottomley 1978a] of the nitric oxide. It has also been suggested that the ν(NO) stretching frequency may be used as a diagnostic measure of the reactivity [Bottomley 1978a]. The generalisation that can be made, is that linear coordinated nitric oxide ligands with an infrared stretching frequency greater than 1890 cm^{-1} are susceptible to attack from nucleophiles such as NH_3 and OH^-, whereas linear nitric oxide ligands with stretching frequencies less than 1850 cm^{-1} are inert to attack from nucleophiles [Bottomley et al. 1973]. Bent coordinated NO is suceptible to attack from electrophiles.

Free nitric oxide reacts with coordinated nitric oxide leading to the formation of nitro complexes [Bhaduri et al. 1981; Clarkson & Basolo 1973; Trogler & Marzilli 1974; Kubota & Phillips 1975; Gwost & Caulton 1974; Diamantis & Sparrow 1969]. This involves an electrophilic attack by free nitric oxide on the bent coordinated nitric oxide through the oxygen atom, followed by reaction with a furthur nitric oxide molecule leading to the disproportionation

products nitrogen dioxide (still coordinated) and dinitrogen oxide. Attack by free nitric oxide on coordinated nitric oxide through the nitrogen end of the free ligand leads to the formation of coordinated dinitrogen oxide [Gwost & Caulton 1974; Bottomley 1978a].

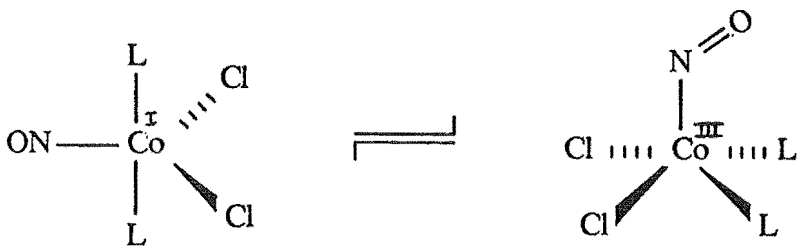
The technique of X-ray photoelectron spectroscopy has been used to study the electron density on the nitrogen atom of coordinated nitric oxide. The nitrogen 1s electron binding energy was found to be sensitive to the electron density on the nitrogen atom. [Chan-Cheng Su & Faller 1975; Finn & Jolly 1972; Pierpont et al. 1971; Clark et al. 1977; Brant & Feltham 1979; Feltham & Brant 1982; Nefedov et al. 1975]. In these studies an attempt was made to use the binding energies as an alternative diagnostic method to infrared spectroscopy to decide the mode of coordination of the nitric oxide. No simple correlation was observed and the authors concluded that whereas bent coordinated nitric oxide ligands show low nitrogen 1s binding energies, linearly coordinated nitric oxide may display either low or high values. For some complexes the results indicated that there was a higher electron density on the nitrogen in the linear mode than in the bent mode. This is a surprising observation because when NO is coordinated in the bent mode there is a lone pair on the the nitrogen atom. The similarity in electron density on the nitrogen atoms in the two complexes may be explained by variations in the π-back-bonding mentioned previously. If there is considerable π-back-bonding in a linearly coordinated nitric oxide ligand this would build up the electron density on the nitrogen atom and thus reduce the nitrogen 1s electron binding energy. Also in the bent case there is the possibility of a π-back-bond in the reverse direction from the electron rich nitrogen atom into a suitable metal orbital such as the

dz^2. This would lead to a reduction in the electron density on the nitrogen so that conceivably the situation could arise in which the electron density on the nitrogen atom for bent and linearly coordinated NO ligands was quite similar.

Attempts have been made to relate the nitrogen 1s binding energies to the position of the V(NO) absorbance in the infrared spectrum [Finn & Jolly 1972] and some correlation has been observed. However the best generalisation that can be made is that when the ν(NO) is low so is the nitrogen 1s binding energy although there are exceptions [Brock et al. 1973; Finn & Jolly 1972]. The fact that this correlation is not fully consistent may be related to the fact that the electron density will be delocalised into the NO system rather than being wholely resident on the nitrogen atom.

A further feature of coordinated nitric oxide that has been reported is hybridisational tautomerism [Collman et al. 1971]. This involves a intramolecular redox reaction in which the coordinated nitric oxide in solutions of the complex exists in equilibrium between the bent and linear forms of coordination. This type of equilibria is shown in Scheme 2.1.

The authors observed this phenomenon for several transition metals including ruthenium. The evidence was based on the observation of two absorbances in the solution infrared spectrum of a complex that contained only one nitric oxide ligand. A low temperature infrared study found a change in the ratio of the two absorbances with temperature whilst the total absorbance remained the same. This was interpreted as a shifting of the equilibria from one tautomeric form to the other due to their differing stabilities with respect to temperature.



SCHEME 2.1

Hybridisational tautomerism of nitric oxide

2.3 OTHER LIGANDS

2.3.1 Introduction

The other ligands studied in this work were, organosulphides, organoarsines, organostibines, and organophosphines. The bonding in these ligands is similar and the description of the bonding for the above ligands is limited to organosulphide and organophosphine ligands, and their oxides. The interaction of these types of ligands with transition metals is often described in terms of Pearson's hard and soft acid and base theory [Pearson 1963; Huheey 1975b; Moeller 1982]. In this theory the ligands and metal centres are classified as hard or soft acids and bases in the Lewis sense [Pearson 1963]. The hard acids and bases are type (a) metal ion or ligands and tend to be small weakly polarised species. The soft acids and bases are class

(b) metal ions and ligands and are larger and more easily polarised [Aharland et al 1958]. Pearson (1963) made the generalisation that like prefers like so that hard metals such as Li^+ will form stable compounds with hard ligands such as F^-. Many of the acids and bases are not easily classified so that the rules can only be used as a guide.

Molecular orbital concepts are useful in explaining these somewhat empirical rules. For the soft ligand and metal centre interaction, the presence of π-bonding is thought to contribute to the stability of these complexes [Chatt 1958; Huheey 1975a; Venanzi 1968]. This occurs when the metal is in a low oxidation state and has many d electrons and π-donation from the metal could be into either a π^* orbital or vacant d orbital on the ligand. This idea may also be used to explain the hard acid hard base interaction in which some π-bonding may still occur but in this case with the ligand donating electron density into vacant metal d orbitals particularly when the metal is in a high oxidation state.

2.3.2 Organosulphide and Organophosphine Ligands

In organosulphide ligands R_2S the sulphur atom is considered to be sp^3 hybridised and thus the ligand bonds to the metal centre forming a covalent bond by overlap of one of its lone pairs and a metal orbital of suitable energy and geometry with the added possibility of some π-type back-bonding into the vacant d orbital of the sulphur atom. A similar situation exists for the organophosphine ligands R_3P.

For the free organosulphoxides and organophosphine oxides the S-O or P-O bonding is typical of that found in the elements of the 2nd short period. These elements show a poor tendency to form O_p-X_p π-bonds but do form $O_p \rightarrow X_d$ dative π-bonds [Allinger et al. 1971; Kirby & Warren 1967; Miller 1972]. The oxygen atom is thought to form a σ-bond and two partial π-back-bonds from the lone pairs into the vacant d orbitals of the phosphorus or sulphur atom so that the overall bond order between the sulphur or phosphorus atom and the oxygen atom is two rather than a maximum of three [Allinger et al. 1971; Bellamy 1968]. That is, there is one covalent bond formed between the sulphur or phosphorus atom and the oxygen from overlap between the sp^3 hybridised sulphur (or phosphorus) atom and the oxygen $2p_x$, and two partial π-bonds from the oxygen back to the sulphur or phosphorus atom equivalent to about one π-bond in all.

In complexes the oxygen is sp^2 hybridised [Emelus & Davies 1981] and a π-bond is formed by overlap of the remaining filled p orbital on the oxygen atom and a vacant d orbital of the sulphur or phosphorus atom. The reported M-L-O bond angles are close to 120° [Fergusson et al 1976]. The presence of a π-system and thus a π^* orbital means there is the possibility of metal π-back-bonding. This explains why sulphoxides can bond to a soft metal centre through the oxygen atom rather than the sulphur atom which might normally be preferred. Steric hinderence may influence which of the atoms is bonded to the metal. It is likely that the oxygen atom is not as good a π-acceptor since in most complexes which contain the strong π-acceptor NO the sulphoxide is usually coordinated opposite the nitrosyl group. If metal to O-S π-back-bonding occurs it will lead to a reduction in the strength of the sulphur oxygen bond due to a build up of electron

density in the S-O π^* orbital. In addition there would be less π-interaction between the oxygen atom and the sulphur because the oxygen atom which is now sp^2 hybridised has only one p orbital available and both of these factors lower the S - O bond order. Support for this comes from the infrared spectra which for Et_2SO shows a shift in the absorbance of the ν(SO) stretching frequency from 1030 cm^{-1} in the free ligand to 920 cm^{-1} in metal complexes [Fergusson & Page 1976; Coll et al. 1986; Coll et al. 1987a] for complexes with oxygen bonded sulphoxide. There is variation in the shift of the ν(SO) in coordinated sulphoxide stretching frequency depending on which atom is bonded to the metal centre [Cotton et al. 1960; Cabeza et al. 1986; Reynolds 1970]. The shift to lower frequency is typical of oxygen bonded complexes. There is a shift to higher frequencies when the sulphoxide ligand is sulphur coordinated. Absorbances as high as 1120 cm^{-1} [Cabeza et al. 1986] and 1088 cm^{-1} [Cabeza & Maitlis 1985] have been reported for ν(SO) in complexes containing coordinated dimethylsulphoxide. Sulphoxides usually absorb in the region of 1040 cm^{-1} [Skattebol et al. 1967] and free dimethylsulphoxide has the ν(SO) absorbance at between 1055 cm^{-1} and 1080 cm^{-1} depending on the solvent [Bellamy 1968; Cotton et al. 1960].

CHAPTER 3

THE PREPARATION AND PHOTOCHEMISTRY OF SOME TRIHALOGENO-(NITROSYL)BIS(ORGANOCHALCOGEN)RUTHENIUM(II) COMPLEXES

3.1 INTRODUCTION

In this chapter the photochemical reactions of ruthenium complexes of the stoichiometric type $Ru(NO)X_3(R_2E)_2$ for X = Cl, Br, and E = S, Se are described. This follows on from work carried out previously in the department [Page 1978; Teow Sian Keong 1981]. The chapter is divided into two parts. In Part A the photochemistry of the organosulphide complexes is described in detail and in Part B a study of the photochemistry of some organoselenide complexes is given. The attempted preparations of some complexes with thionitrosyl, and nitro ligands are also described in Part B.

Prior to the commencement of the experimental work the literature was searched for topics related to this study. The following is a list of relevant review articles.

The chemistry of ruthenium organometallic complexes has been reviewed regularly [McCleverty 1969; McCleverty 1972; McCleverty 1974; McCleverty 1975; McCleverty 1976; McCleverty 1978; McCleverty 1979a; McCleverty 1979b; McCleverty 1981; McCleverty 1984; Reger 1981; Keister 1983; Keister 1984] as has the coordination chemistry of ruthenium [Seddon 1981; Seddon 1985; Seddon 1982].

The chemistry of the transition metals has been reviewed under the headings; nitrosyl complexes or some specialist aspect of the chemistry of complexes containing nitric oxide [Bottomley 1978a; Bottomley 1978b; McCleverty 1979b; Sidgwick & Bailey 1934; Johnson &

McCleverty 1966; Griffith 1968; Addison & Lewis 1955; Moeller 1946a; Moeller 1946b; Enemark & Feltham 1974; Frentz & Ibers 1972; Masek 1969; Eisenberg & Meyer 1975; Connelly 1972; Griffith et al. 1958; Rard 1985], weak donor ligands [Davies & Hartley 1981; Emelus & Davies 1981; Fackler 1976; Kuehn & Isied 1980; Abel et al. 1984; Murray & Hartley 1981; Reynolds 1970], organophosphines and organoarsines [McAuliffe & Levason 1979] and photochemistry [Waltz & Sutherland 1972].

A comprehensive monograph on the chemistry of ruthenium has recently been published [Seddon & Seddon 1984], which covers the literature up to 1978. Griffith (1967) has published a monograph reviewing the chemistry of the four platinum metals ruthenium, osmium, rhodium and iridium. The platinum metals have also been reviewed under the subject of X-ray structures [McDonald 1974; Manojlovic-Muir 1973; Amma 1971] and the preparative and general chemistries [Kane-MaGuire & Clack 1976; Kane-MaGuire 1972].

The significant aspects of the chemistry of the complexes which are discussed in this thesis, are dealt with in more detail in the relevant sections.

Some generalisations can be made from the above survey. Much of the chemistry of ruthenium involves reactions with organometallic ligands, especially organophosphines. Also ruthenium complexes are important as catalysts. The photochemical reactions of ruthenium complexes mainly involve ligand substitution or isomerisation. Oxidation of coordinated ligands is rare but ruthenium complexes are found to catalyse the oxidation of free ligands especially organophosphines.

PART A

THE PHOTOCHEMISTRY OF SOME TRIHALOGENO(NITROSYL)-BIS(ORGANOSULPHIDE)RUTHENIUM(II) COMPLEXES

3.2 A SUMMARY OF THE KNOWN FACTS OF THE PHOTOCHEMISTRY OF TRIHALOGENO(NITROSYL)BIS(ORGANOSULPHIDE)-RUTHENIUM(II) COMPLEXES $Ru(NO)X_3(R_2S)_2$

The oxidation of ligands bonded to transition metal centres has been reported previously [Vaska 1963; Geoffroy et al. 1976a] but there do not appear to be any reports of oxidation of thioethers other than those by previous workers in this department. However, ruthenium complexes have been reported to act as catalysts in the oxidation of alkylsulphides by dioxygen [Riley & Shumate 1984; Muller & Godoy 1983].

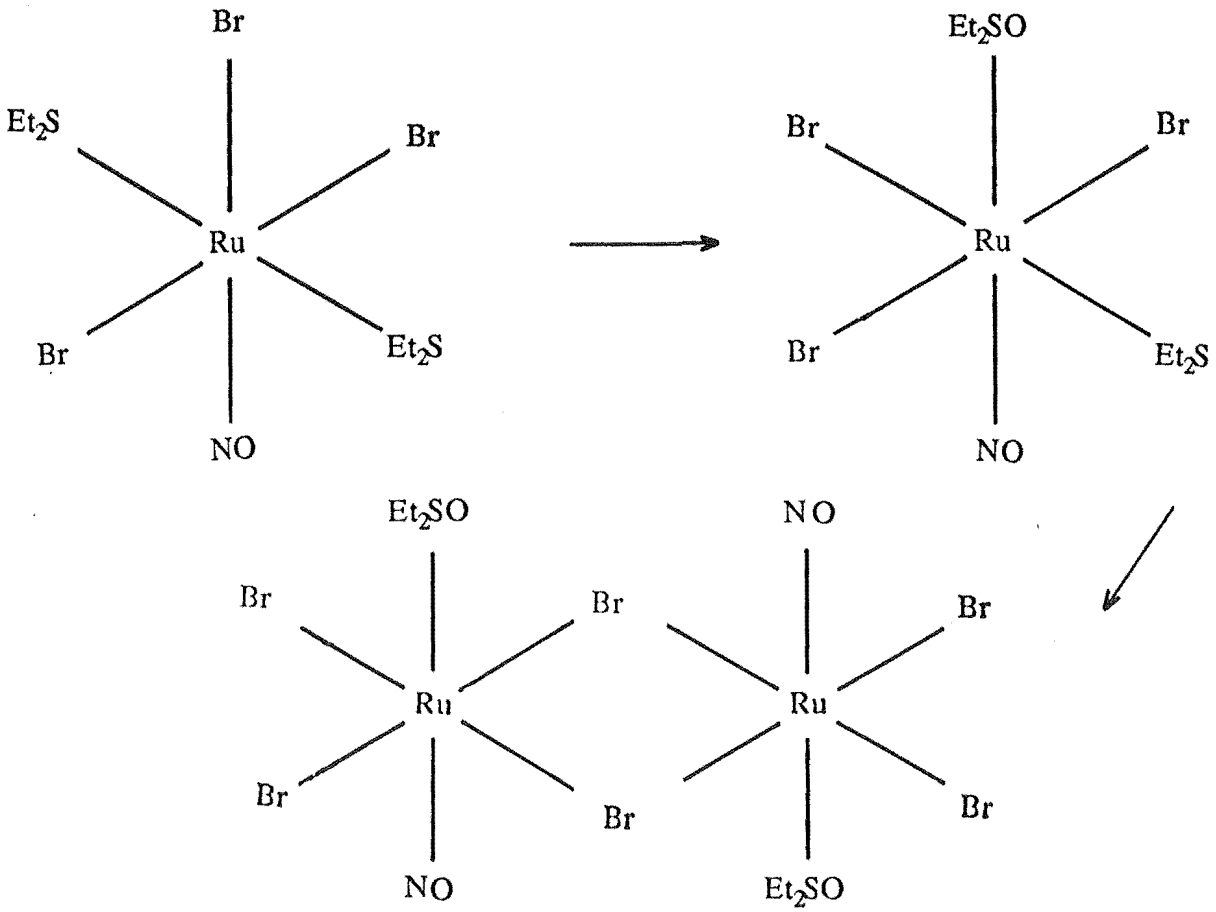
Page discovered that a solution of tribromo(nitrosyl)-bis(diethylsulphide)ruthenium(II) $Ru(NO)Br_3(Et_2S)_2$ in chloroform underwent a colour change upon exposure to sunlight. Further investigation revealed that the reaction probably proceeded in two main steps, firstly the formation of a diethylsulphide diethylsulphoxide complex $Ru(NO)Br_3(Et_2S)(Et_2SO)$, and secondly the formation of a dimeric ruthenium complex $[Ru(NO)Br_3(Et_2SO)]_2$. The overall reaction as given by Page is outlined in Scheme 3.1 and the stereochemical changes in Scheme 3.2. The reaction was followed by both ^1H n.m.r and solution infrared techniques. The ^1H n.m.r spectrum of the initial complex consists of a triplet and a quartet for the CH_3 and CH_2 protons respectively and the reaction path was conveniently followed by the change in the chemical shift of the methylene protons.

	N.M.R.[1]	Infrared[2]
$Ru(NO)Br_3(Et_2S)_2$	3.27 ppm	1860 cm^{-1}
↓ $h\nu/O_2$/10 days		
$Ru(NO)Br_3(Et_2S)_2$	3.27 ppm	1860 cm^{-1}
$Ru(NO)Br_3(Et_2S)(Et_2SO)$	3.20, 3.03 ppm	1880 cm^{-1}
↓ 20 days		
$Ru(NO)Br_3(Et_2S)(Et_2SO)$	3.20, 3.03 ppm	1880 cm^{-1}
↓ two months		
$[Ru(NO)Br_3(Et_2SO)]_2$	insoluble	1878 cm^{-1}*
+ Et_2SO	2.70 ppm	
↓ three months		
$[Ru(NO)Br_3(Et_2SO)]_2$	insoluble	1878 cm^{-1}*
Et_2SO + Et_2SO_2	2.70, 3.00 ppm	

SCHEME 3.1

Overall reaction scheme for the photochemical reaction of $Ru(NO)Br_3(Et_2S)_2$

(1) n.m.r absorbance for the methylene protons
(2) ν(NO) solution infrared
* mull infrared spectrum measured



SCHEME 3.2

Stereochemical changes for the photochemical reaction of $Ru(NO)Br_3(Et_2S)_2$

The change in chemical shift of the methyl protons was less pronounced and was less useful in the study. The infrared spectrum showed a characteristic strong absorbance for the ν(NO), which was observed in solution and in the solid state. Since the reaction was carried out in chloroform it was possible to follow the reaction path using solution infrared. Page also observed a similar reaction for ruthenium complexes containing the organosulphides Me_2S, MeSPh, n-Pr_2S, EtSPh, n-Bu_2S, Et_2Se, and EtSePh as well as for other halogen complexes, X = Cl, I with diethylsulphide. For the organosulphide ligands Page found evidence for the formation of an organosulphide organosulphoxide complex, but the dimer was only observed in a few cases. He also observed a colour change for the organoselenide complexes upon exposure to sunlight, but did not isolate any reaction products or study the reaction furthur.

Teow Sian Keong studied the early part of the reaction in more detail (i.e. when the colour change was first observed), which is some time before the complexes discussed above are isolated. Teow Sian Keong showed that the intial colour change is due to the formation of a ruthenium(III) complex which was isolated as $RuBr_3(Et_2S)_3$ when an excess of Et_2S was present. A summary of the known facts of the photochemical reactions of the trihalogeno(nitrosyl)bis-(organochalcogen)ruthenium(II) complexes as studied by both Page and Teow Sian Keong is given in Table 3.1.

The work undertaken in this thesis involved furthur investigation and extension of the above work.

(A) Reaction rate increased by;

i) excess diethylsulphide
ii) acetic acid
iii) ethanol
iv) use of dioxygen saturated chloroform

(B) Reaction rate inhibited by;

i) free radical scavengers
ii) removal of dioxygen from chloroform
iii) use of ethanol free chloroform
iv) increased concentration of complex in solution

(C) UV-visible spectrum of early stages of reaction is similar to that of a solution of trihalogenotris(organosulphide)ruthenium(III) in chloroform

(D) Tris-organosulphide complex isolated from solution in presence of excess ligand for Et_2S, $(n\text{-}Pr)_2S$, $(n\text{-}Bu)_2S$

(E) Tris-organosulphide complex reacts with nitric oxide gas to form original nitrosylbis(organosulphide) complex

(F) Light is required for the reaction and is most effective for λ = 380 - 480 nm

TABLE 3.1

Summary of the known facts for the photochemical reaction of trihalogeno(nitrosyl)bis(organosulphide)ruthenium(II) $Ru(NO)X_3(R_2S)_2$

3.3 FREE LIGAND STUDIES

3.3.1 Introduction

In order to understand the photochemical reaction more fully, a study was made of the oxidation of uncoordinated diethylsulphide and some other organosulphides. In order to identify the reaction products, the compounds diethylsulphoxide and diethylsulphone were synthesised by reported methods [Johnson & Keiser 1966; Harville & Reed 1968; Walling & Mintz 1967]. Their ^{1}H n.m.r spectra were recorded (Table 3.5 in the experimental section) and found to agree well with literature values [Est-Stammer & Engberts 1973; Kitching et al. 1969; Kitching et al. 1970; Robinson 1961; Tamres & Searles 1959].

A summary of the reactions of Et_2S and other organosulphides with different oxidising agents is given in Table 3.2.

3.3.2 Autooxidation of Organosulphides

Oxidation of alkylsulphides by dioxygen has been well studied and is termed autooxidation [Bateman & Cunneen 1955; Bateman & Shipley 1955; Bateman et al. 1956; Bateman et al. 1957; Barnard et al. 1961]. This term will be used but it is an unsual name since the oxidising agent is the dioxygen. The reaction requires a free radical initiator, such as radiation of a suitable wavelength, and a protic solvent [Foote & Peters 1971; Correa & Riley, 1985]. Autooxidation has been reported to be catalysed by ruthenium(II) or ruthenium(III) complexes [Muller & Godoy 1983; Henbest & Trocha-Grimshaw 1974; Ledlie et al. 1976; Riley & Shumate 1984]. Since Page and Teow Sian Keong carried out their studies of the ruthenium complexes in solvent grade

(A) NO or O_2 alone will not oxidise Et_2S

(B) NO + O_2 or NO_2 at room temperature easily oxidises R_2S to R_2SO and onto R_2SO_2 for R = Et_2S, $(n\text{-}Bu)_2S$, (Me)SPh, (Et)SPh, (n-Pr)SPh, and (n-Bu)SPh

(C) Et_2S + NO/O_2 or NO_2 at low temperature (-5 °C) gives Et_2SO

(D) Et_2S + O_2/hν/protic solvent/room temperature → Et_2SO + Et_2SO_2

(E) Et_2S + $NO/Ru(III)/CHCl_3$ → no reaction

(F) Et_2S + $O_2/Ru(III)/CHCl_3$ → no reaction

(G) Et_2S + $O_2/Ru(III)/CHCl_3/h\nu$ → Et_2SO

TABLE 3.2

Summary of the reactions of free ligands with different oxidising agents

chloroform which contains some ethanol as a stabiliser [Perrin et al. 1981], and because the the oxidation of R_2S requires protic solvents, the oxidation of Et_2S by O_2 in the presence of radiation was attempted in solvent grade chloroform. However, no oxidation occurred as indicated by the ^1H n.m.r. and infrared spectra. Hence it appears that the level of ethanol present in solvent grade chloroform is insufficient for the autooxidation of this level of Et_2S (1ml) in chloroform (50ml). When more ethanol was added to the chloroform (2ml to 50ml of chloroform) the autooxidation proceeded smoothly.

Since Teow Sian Keong had discovered that a Ru(III) product formed in the early stages of the photooxidation reaction of $Ru(NO)Br_3(Et_2S)_2$, it was of interest to see if this complex would achieve the autooxidation of Et_2S to Et_2SO. Oxidation of Et_2S did now occur in reagent grade chloroform, but only when the solution was also irradiated. The rate of the oxidation was comparable to the autooxidation of diethylsulphide in ethanol as estimated by the time taken to produce diethylsulphoxide.

3.3.3 Oxidation of Organosulphides by Nitrogen Oxides

As outlined in Table 3.2 oxidation of diethylsulphide to diethylsulphoxide or diethylsulphone is easily achieved using either NO_2 or a mixture of NO and O_2. Similar reactions also occurred for the organosulphides $n\text{-}Bu_2S$, MePhS, EtPhS, n-PrPhS, n-BuPhS and Ph_2S. The oxidation of organosulphides by NO_2 has been reported previously but under different conditions viz. at low temperatures (ca. -70 ^oC) and in different solvents [Addison & Sheldon 1956; Pummerer 1910; Sandler & Karo 1968; Goheen & Bennett 1961; Horner & Hubenett 1953;

Grosjean 1984]. The main reaction product reported was the organosulphoxide.

The oxidation reactions observed in this work were faster than the autooxidation reactions, and the main product was the organosulphone. Only when the reaction was carried out at low temperature (ca. -5.0 ^{o}C) could the organosulphoxide be isolated. At lower temperatures (ca. -40 ^{o}C) in chloroform no oxidation occurred.

If pure NO was used by itself in the reaction no oxidation was observed. This has been reported previously [Longhi et al. 1962].

3.4 MASS SPECTROMETRIC STUDIES OF THE PHOTOCHEMICAL OXIDATION OF TRIBROMO(NITROSYL)BIS(DIETHYLSULPHIDE)RUTHENIUM(II)

3.4.1 Introduction

Since studies on the free ligand indicated that the oxidation of diethylsulphide may be accomplished with either NO_2 or NO/O_2, a study was undertaken of the complex $Ru(NO)Br_3(Et_2S)_2$ using mass spectrometric methods to analyse the gaseous reaction products. If the coordinated NO was involved, this would require its loss from some of the complex. Whilst loss of nitric oxide from complexes of ruthenium in reactions is not unknown, it is certainly not common. Nitric oxide has traditionally been regarded as an inert ligand when bonded to Ru(II) (t^6_{2g}) [Addison & Lewis 1955; Griffith 1967]. Radiation is required to bring about the loss of nitric oxide from ruthenium complexes [Nikol'skii et al. 1976; Cox & Wallace 1971].

3.4.2 Mass Spectrometric Results

In order to detect whether or not free nitric oxide was produced in the photochemical oxidation, the gas above the reaction mixture was analysed using a microprocesser controlled SMS DATAQUAD Quadrupole Mass spectrometer. The analytical results together with an accurate mass determination of the peak at mass 30 (using the AEI MS 902) established that nitric oxide gas was produced at the early stages of the irradiation. Found mass 29.99794; Calculated for NO 29.99799. The results of the mass spectrometer studies are summarised in Table 3.3.

A peak at mass 30 could also arise from NO_2 by interaction with the 70 eV electrons in the mass spectrometer [Stenhagen et al. 1969]. The mass spectrum for NO_2 has two peaks, one at mass 30 and another of one third of the intensity at mass 46. In some reactions a small increase in the peak at mass 46 was observed, but it was smaller than that expected for NO_2 based on the peak at mass 30. In some experiments the reaction solution was cooled to ca. $-105^{\circ}C$ before gas analysis, and at this temperature NO_2 would be frozen out.

The accurate mass determination was necessary since the SMS DATAQUAD mass spectrometer measures only integral mass values. Another possible gaseous product is ethane which would also have an integral mass of 30. Ethane could be produced in the reaction by oxidation as outlined in Scheme 3.3.

(A) Nitric oxide gas liberated upon irradiation of the complex

(B) Nitric oxide continues to be liberated with continuing irradiation of the complex

(C) Nitric oxide liberated in the presence or absence of dioxygen

(D) The amount of nitric oxide liberated increases when diethylsulphide is present in excess

(E) No nitric oxide was liberated in a control experiment for which there was no irradiation of the complex

(F) Accurate mass for mass 30 is 29.99794 (Calculated for NO = 29.99799; Calculated for C_2H_6 = 30.046948)

(G) Mass spectrometer experiments for free ligand oxidation reactions by NO/O_2 or NO_2 show no evidence for N_2O, or N_2 but show evidence for NO

TABLE 3.3

Summary of the mass spectrometric studies of the photochemical reaction of
tribromo(nitrosyl)bis(diethylsulphide)ruthenium(II)
$Ru(NO)Br_3(Et_2S)_2$

$$R_2S + NO^{\bullet} \rightarrow R\text{-}S\text{-}NO + R^{\bullet} \quad (1)$$

$$R^{\bullet} + R_2S \rightarrow R\text{-}R + R\text{-}S\text{-}R^{\bullet} \quad (2)$$

SCHEME 3.3

Free radical oxidation of diethylsulphide

The final step in Scheme 3.3 involves hydrogen abstraction, probably from another diethylsulphide ligand. It is unlikely that the ethane is produced from photochemical reduction of ethanol [Coxon & Halton 1974] since the reaction conditions are oxidising and the oxidation of the diethylsulphide by the $NO^{\bullet}$ radical is more likely. Also the accurate mass determination is not consistent with ethane. Found: Mass 29.99794; Calculated for C_2H_6 30.046948.

3.4.3 Source of the Nitric Oxide

Nitric oxide has been reported as being formed from the direct combination of the elements. However, this requires high temperatures and pressures and the reaction is unlikely to occur under the conditions used in this study [Jones 1973; Fergusson 1982]. Thus the most likely source of the NO is the ruthenium complex.

When a solution of the complex in O_2 free chloroform was irradiated there was evidence in the mass spectrum for NO. This suggests that O_2 is not required for the loss of NO.

The amount of nitric oxide lost by the complex is likely to be quite small since there is no significant change to the ^{1}H n.m.r spectrum in the early stages of the reaction and no evidence of free nitric oxide in the solution infrared spectrum. A new absorbance at 1880 cm^{-1} does appear later in the experiment and this is in the correct region for V(NO) for free nitric oxide [Cotton & Wilkinson 1972; Nefedov et al. 1975]. However, this absorbance has been attributed to coordinated NO in the complex $Ru(NO)Br_3(Et_2S)(Et_2SO)$ [Page 1978; Teow Sian Keong 1981].

3.4.4 Amount of Nitric Oxide Lost from the Complex

To establish how much nitric oxide was lost from the complex the volume of gas liberated by the reaction was measured on a gas vacuum line of known volume using a McLeod gauge that had been calibrated with a MKS Baratron Capacitance Manometer (see Chapter 11). If all the gas liberated was nitric oxide (which is probably unlikely), then it is less than two percent of the total nitric oxide in the complex. Raoult's Law states that the vapour pressure of a pure solvent is greater than that of the solvent in a solution i.e.

$$P_{solution} = X_1 P^{O}$$

where P^{O} = vapour pressure of the pure solvent

and X_1 = mole fraction.

Since the amount of gas liberated from the photochemical oxidation was estimated from the difference between the amount of gas above the solution and a blank of just chloroform this means that it is possible that there is more gas produced than suggested from the difference in gas pressures. However, since the formula weight of the ruthenium complex is high (551.16), and only 0.18g of the complex was used in 10ml, the mole fraction of chloroform in the solution is close to that of pure chloroform.

3.4.5 Other Gaseous Products

Initial analysis of the gaseous reaction products of the oxidation of diethylsulphide with nitrogen oxides and of the photooxidation reaction of the complex $Ru(NO)Br_3(Et_2S)_2$ using the AEI MS 902 indicated that N_2 was one of the reaction products. There have been some reports of nitrogen oxides acting as oxidising agents and being reduced to N_2 [Buckingham et al. 1963; Cooper et al. 1970; Heiber & Karamolowsky 1963; Banks et al. 1968; Banks et al. 1967; Diamantis & Sparrow 1970]. In these reactions there was another source of nitrogen (such as a second NO group), or the oxidising agent was NO. The oxidation of Et_2S by NO/O_2 was therefore carried out in an argon atmosphere and in this case there was no evidence for the production of N_2.

The conclusion from this experiment was that the AEI MS 902 mass spectrometer was unsuitable for carrying out contolled measurement of gaseous samples. In the experiments using the SMS DATAQUAD mass spectrometer, any increase in the level of dinitrogen was found to be accompanied by an increase in the dioxygen level, and this probably

means that an increase in the amount of air in the system has occurred.

3.5 PROPOSED MECHANISM FOR THE PHOTOCHEMICAL OXIDATION OF TRIBROMO(NITROSYL)BIS(DIETHYLSULPHIDE)RUTHENIUM(II)

3.5.1 Mechanism

The reactions outlined in Scheme 3.4 are proposed as being the most reasonable interpretation of the overall results. The initial step involves photochemical excitation of the complex and subsequent loss of a small amount of nitric oxide ligand, which then combining with the dissolved dioxygen in solution to form some nitrogen dioxide, brings about the oxidation of the diethylsulphide to diethylsulphoxide. This regenerates the NO which is therefore effectively a catalyst in the oxidation.

3.5.2 Step 1

Step 1 involves the excitation of the complex by radiation to an excited electronic state. In a control experiment in which the complex was not irradiated no nitric oxide gas was detected. Hence this suggests that the radiation is involved in the loss of the nitric oxide ligand. Either sunlight or radiation from a mercury discharge lamp are suitable sources, the most effective radiation being 460-480 nm [Teow Sian Keong 1981] which corresponds to the position of the $^1A_1 \rightarrow {}^1T_1$ transition [Figgis 1966]. In the electronically excited state $^1T_1$, the ruthenium may be less firmly bound to the NO group, as there is now some electron density in the e_g^* orbitals and therefore

$$Ru(NO)Br_3(Et_2S)_2 + h\nu \rightarrow Ru(NO)Br_3(Et_2S)_2^* \quad [1]$$

$$Ru(NO)Br_3(Et_2S)_2^* + Et_2S \rightarrow RuBr_3(Et_2S)_3 + NO \quad [2a]$$

$$Ru(NO)Br_3(Et_2S)_2^* + Solv \rightarrow RuBr_3(Et_2S)_2(Solv) + NO \quad [2b]$$

$$RuBr_3(Et_2S)_3 + NO \rightarrow Ru(NO)Br_3(Et_2S)_2 + Et_2S \quad [3a]$$

$$RuBr_3(Et_2S)_2(Solv) + NO \rightarrow Ru(NO)Br_3(Et_2S)_2 + Solv \quad [3b]$$

$$NO + NO + O_2 \rightarrow 2\ NO_2 \quad [4]$$

$$Ru(NO)Br_3(Et_2S)_2 + NO_2 \rightarrow Ru(NO)Br_3(Et_2S)(Et_2SO) + NO \quad [5]$$

SCHEME 3.4

Proposed mechanism for the photochemical reaction of $Ru(NO)Br_3(Et_2S)_2$

Solv = electron donating solvent molecule

less available in the t_{2g} orbitals for Ru to NO dative π-bonding. The presence of electrons in the e_g^* orbitals also leads to a build up of electron density along the axes, which results in additional bond weakening due to repulsion with the negatively charged ligands.

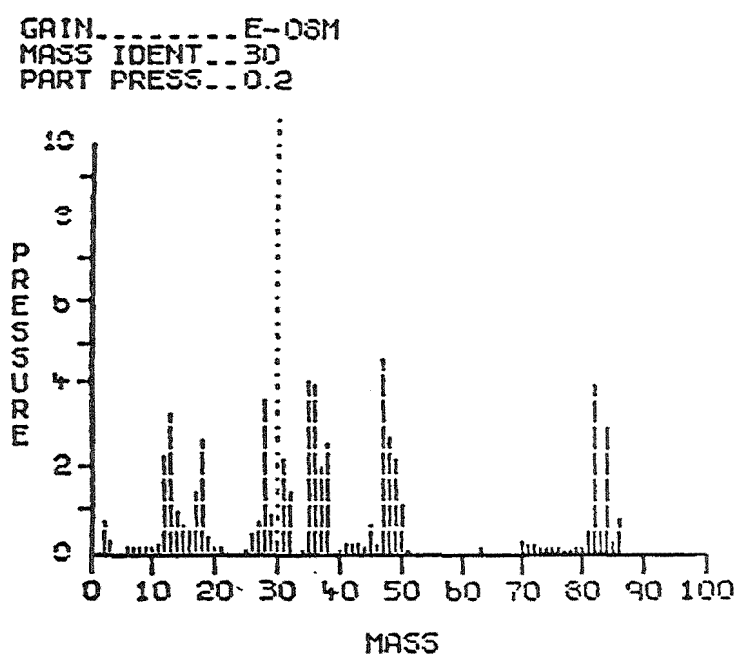
3.5.3 Step 2

In Step 2 the electronically excited complex loses NO and forms a Ru(III) species. This is a redox reaction with the ruthenium losing an electron going from Ru(II) to Ru(III) and the NO^+ gaining an electron forming neutral $NO^{\bullet}$.

It is likely that the role of ethanol in the chloroform is to provide the sixth ligand for the Ru(III) species that is formed when some of the NO ligand is lost from the original complex. The addition of free diethylsulphide speeds up the reaction, presumably by more effectively replacing the lost NO ligand and forming $RuBr_3(Et_2S)_3$. Two examples of the mass spectral results are given in Figure 3.1. In Figure 3.1(A) the spectrum is for chloroform only, and in 3.1(B) for the complex dissolved in chloroform. Both spectra were obtained after irradiation for 90 minutes. The spectrum obtained when an excess of diethylsulphide was added to the system is shown in Figure 3.2. It is clear that more nitric oxide was liberated in this experiment for the same radiation time.

Teow Sian Keong (1981) studied the rate of the photochemical reaction of other organosulphide complexes of ruthenium(II). The results of his work are summarised in Table 3.4. The UV-visible spectral studies correspond to the formation of the Ru(III) species. The chloro- complex $Ru(NO)Cl_3(Et_2S)_2$ was also studied in the present

(A)



(B)

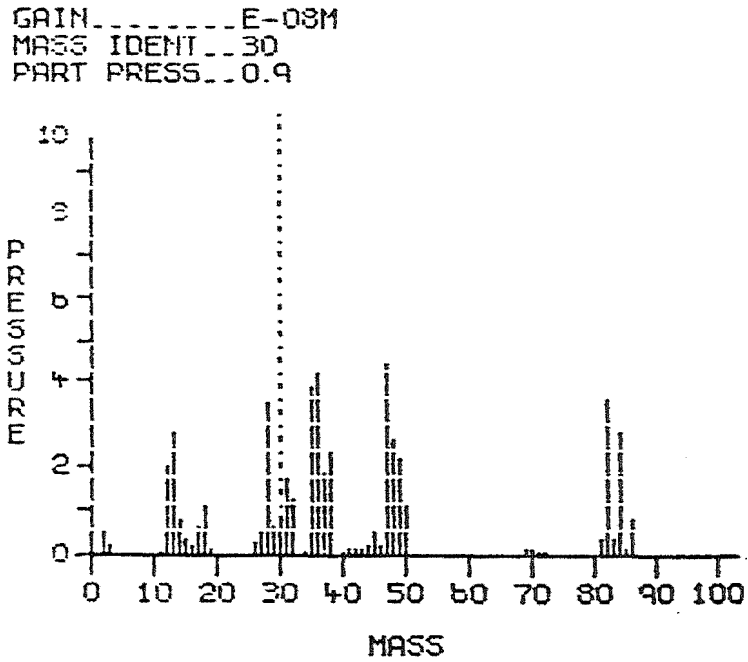


FIGURE 3.1

(A) mass spectrum for chloroform

(B) mass spectrum for solution of $Ru(NO)Br_3(Et_2S)_2$ *after irradiation*

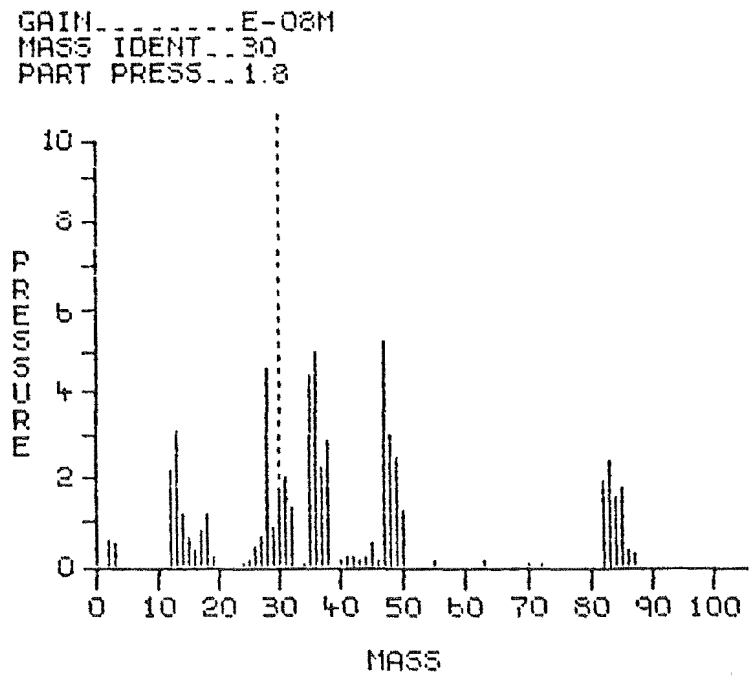


FIGURE 3.2

Mass spectrum for $Ru(NO)Br_3(Et_2S)_2$ *after irradiation for 90 minutes in the presence of excess* Et_2S

(A) ^{1}H n.m.r. studies showed an increase in the reaction rate in the order I > Br > Cl for Et_2S

(B) Solution infrared studies showed;

i) Br > I for Et_2S

ii) $(iso\text{-}Bu)_2S$ > $(n\text{-}Pr)_2S$ > Et_2S

for X = Cl, Br.

(C) UV-visible spectroscopy studies showed;

i) Et_2S > $(n\text{-}Pr)_2S$ > $(iso\text{-}Bu)_2S$ for X = Cl, Br

ii) Cl > Br > I for Et_2S

iii) (n-Bu)SPh > (n-Pr)SPh > EtSPh for Br

TABLE 3.4

Summary of the influence of ligand variation on the rate of the photochemical reactions of $Ru(NO)X_3(R_2S)_2$ complexes

work. It was discovered using the SMS DATAQUAD mass spectrometer that the nitric oxide was lost more easily than for the bromo- complex. The mass spectrum obtained after irradiation for only 45 minutes is given in Figure 3.3. The spectrum shows that a greater amount of NO was produced for the shorter irradiation time.

The mass spectromeric study and Teow Sian Keong's results suggest that the loss of the NO from the complex proceeds by an initial associative step (Scheme 3.5) with the formation a seven coordinate complex. This seven coordinate complex would lose NO to form the tris-organosulphide complex or a complex containing ethanol. The reaction rate would be slower in the presence of bulky ligands on the initial complex, and faster when the attacking species (R_2S or EtOH) was present in excess.

3.5.4 Step 3

Step 3 is the reverse of Step 2. Teow Sian Keong has shown that NO will react with the complex $RuBr_3(Et_2S)_3$ in the dark replacing one of the Et_2S ligands to form the complex $Ru(NO)Br_3(Et_2S)_2$.

3.5.5 Step 4

In Step 4 the NO produced from the complex reacts with O_2 and is oxidised to NO_2. For the oxidation of the Et_2S to to Et_2SO to occur by the reaction given in Step 5, the rate of the reaction in Step 4 needs to be faster than that in Step 3. Even though the characteristic brown colour of NO_2 is readily observed when O_2 and NO are mixed, this can be deceptive since the reaction in the gas phase at least is relatively slow with a third order rate constant of

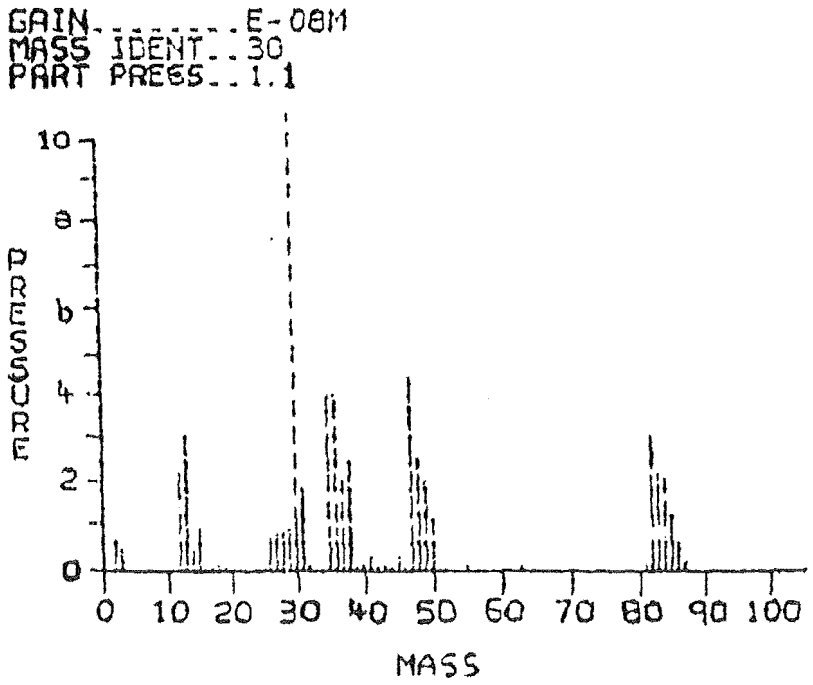
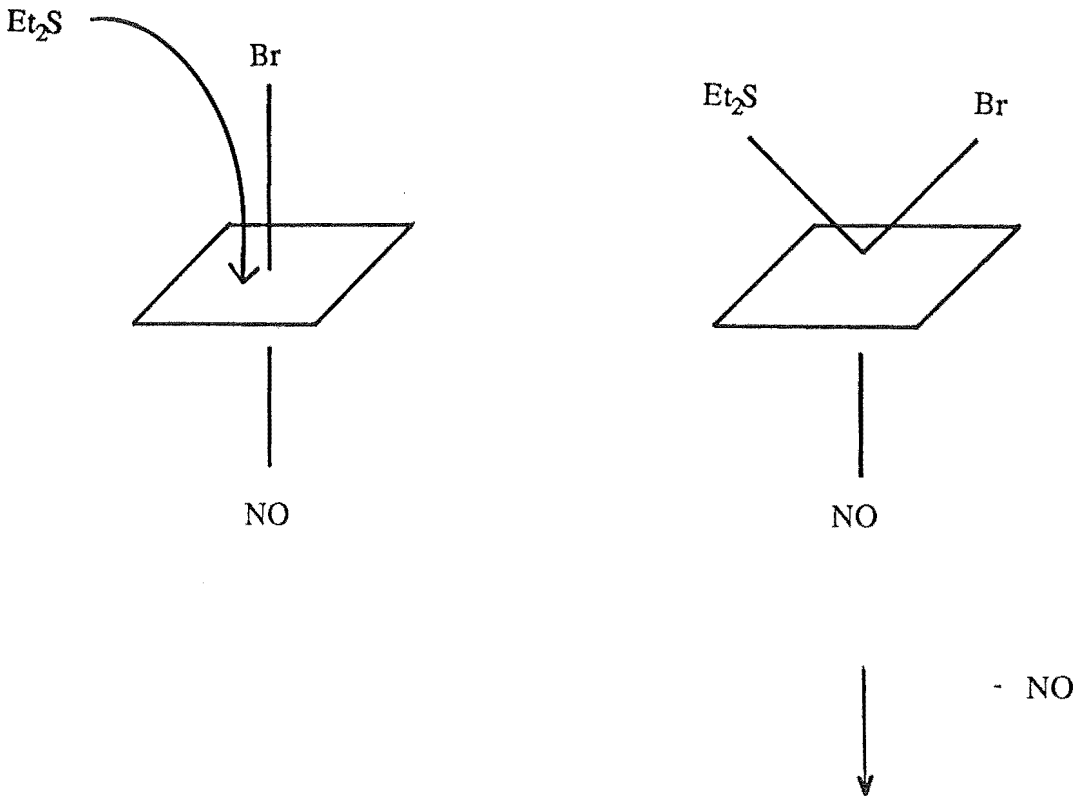


FIGURE 3.3

Mass spectrum for $Ru(NO)Cl_3(Et_2S)_2$
after irradiation for 45 minutes

$Ru(NO)Br_3(Et_2S)_2 + h\nu \longrightarrow Ru(NO)Br_3(Et_2S)_2^*$



i) RATE SLOW FOR BULKY LIGANDS

ii) RATE FASTER FOR ELECTRON DONOR PRESENT

SCHEME 3.5

Mechanism for the formation of the tris-organosulphide complex $RuX_3(R_2S)_3$

3.3×10^{-39} $cm^6 sec^{-1}$ [Hampson & Garvin 1977]. However, as previously shown (Section 3.3), a mixture of NO and O_2 will oxidise free diethylsulphide, and this supports the scheme.

Based on the infrared absorbance of ν(NO) at 1860 cm^{-1} it is likely that the nitric oxide is coordinated in the linear mode in the complex $Ru(NO)Br_3(Et_2S)_2$. This means that there is little likelihood of the nitric oxide being oxidised whilst still attached to the ruthenium atom as has been reported for some complexes where NO is coordinated in the bent mode [Eisenberg & Meyer 1975; Masek 1969; Bottomley et al. 1973]. The electron density on the nitrogen atom will be increased due to the π-back bond of the ruthenium d electrons into the NO π^* system, but this is probably insufficient to to allow attack by an electrophile.

There was no evidence for hybridisational tautomerism in the reaction. In hybridisational tautomerism the NO goes from being bound as NO^+ to NO^- (Chapter 2). There was no evidence seen in the infrared spectra (solution or solid state) at any stage of the reaction for the presence of bent coordinated NO.

Consequently the oxidation of the nitric oxide to the nitrogen dioxide probably occurs in the gas phase above the solution or in the solution. The radiation may also assist at this stage as it has been reported that radiation increases the rate of reaction between NO and O_2 [Heicklen & Cohen 1968].

3.5.6 Step 5

i) Oxidation of Et_2S to Et_2SO

In Step 5 the NO_2 reacts with the complex and oxidises one of the Et_2S ligands to Et_2SO. Whereas this step requires dioxygen, Step 2 does not. Hence the oxidation of the Et_2S should be possible if nitric oxide and dioxygen, or nitrogen dioxide, are added to a chloroform solution of $Ru(NO)Br_3(Et_2S)_2$ in the dark. Oxidation was in fact achieved when controlled small amounts of the gases were added, and the products obtained were the starting material, and the diethylsulphide diethylsulphoxide ruthenium complex $Ru(NO)Br_3(Et_2S)(Et_2SO)$. Also during attempts to prepare a nitro complex of ruthenium(II) (Section 3.10), pure NO_2 was bubbled through a boiling solution of $RuCl_3.3H_2O$ and Et_2S in chloroform, and this produced the diethylsulphide diethylsulphoxide complex.

The ethanol was not required for Step 5, since when nitric oxide and dioxygen were added to an ethanol free chloroform solution of the complex in the dark, oxidation of the Et_2S still occurred.

ii) Stereochemical changes

The oxidation of the diethylsulphide may occur whilst the ligand is still attached to the ruthenium atom. However, stereochemical rearrangement occurs, as the stereochemistry changes from a trans bis-diethylsulphide complex to a cis diethylsulphide diethylsulphoxide complex (Scheme 3.2) [Fergusson et al. 1976].

Teow Sian Keong (1981) studied the rate of the formation of a number of organosulphide organosulphoxide complexes using ^1H n.m.r. and

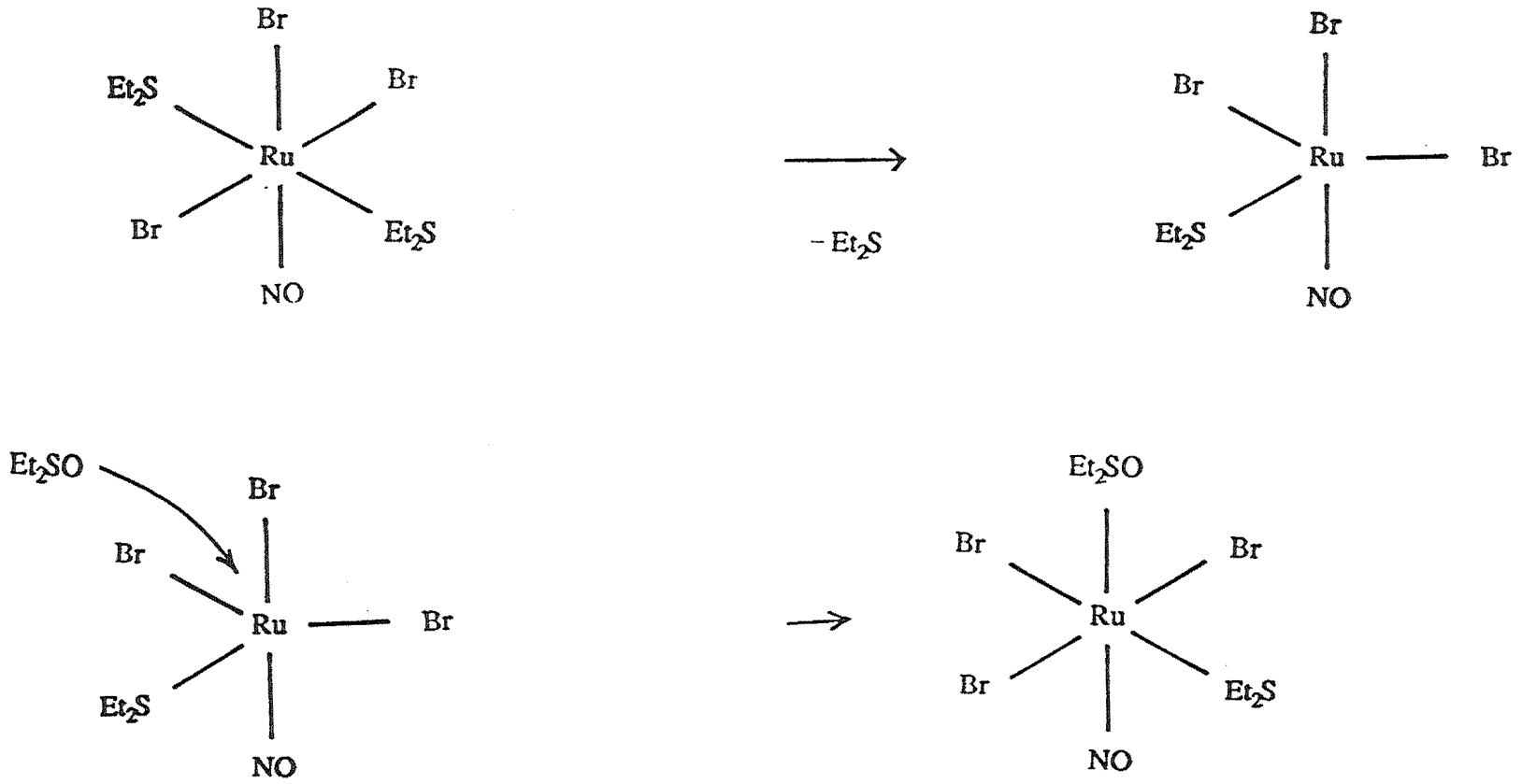
infrared spectroscopy for different ligands. His results are given in Table 3.4. There seems to be some inconsistency between the results of the ^{1}H n.m.r. study and the solution infrared study and the results do not aid in elucidating the mechanism of this step. It is possible that the reaction goes by different mechanisms for different complexes. The stability or solubility of the complex may influence the rate of the formation of the organosulphide organosulphoxide complex.

The stereochemical changes observed may occur via a dissociative mechanism. This would lead to the formation of a five coordinate trigonal bypyridimal intermediate as shown in Scheme 3.6(A). Attack at the position indicated would lead to products with the observed stereochemistry.

An associative mechanism is also possible (Scheme 3.6(B) & 3.6(C)) and could proceed by either direct formation of the complex in the correct stereochemical arrangement, or with rearrangement occurring in a subsequent step.

3.5.7 Formation of the Dimeric Ruthenium Complex

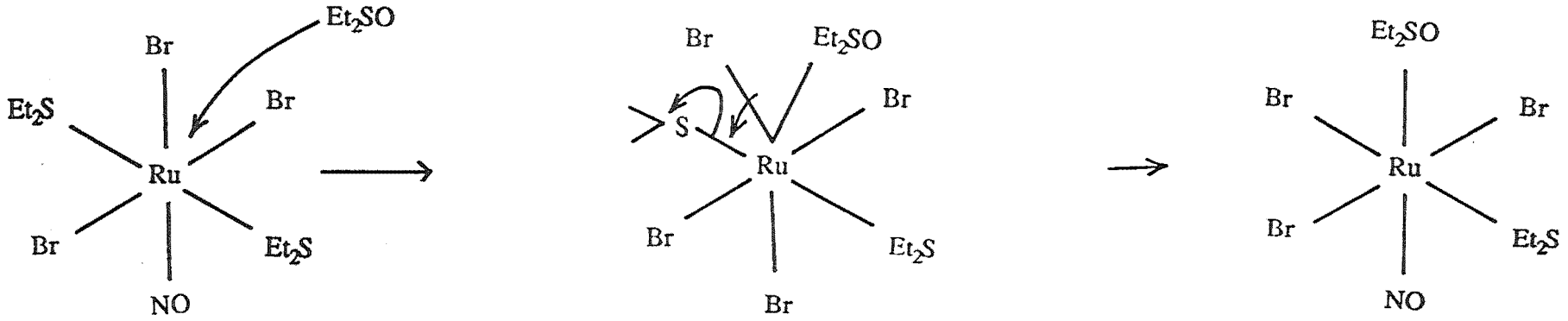
Since the stereochemical arrangement of the ligands present in the organosulphide organosulphoxide complex is retained in the dimeric ruthenium complex, the dimerisation step may occur as illustrated in Scheme 3.7. Page (1978) observed the formation of the dimer only some time after the formation of the organosulphide organosulphoxide complex. The relatively low solubility of the organosulphide organosulphoxide complex may be the reason for the slow formation of the dimer.



SCHEME 3.6

Proposed mechanism for the formation of the organosulphide organosulphoxide complex $Ru(NO)X_3(Et_2S)(Et_2SO)$

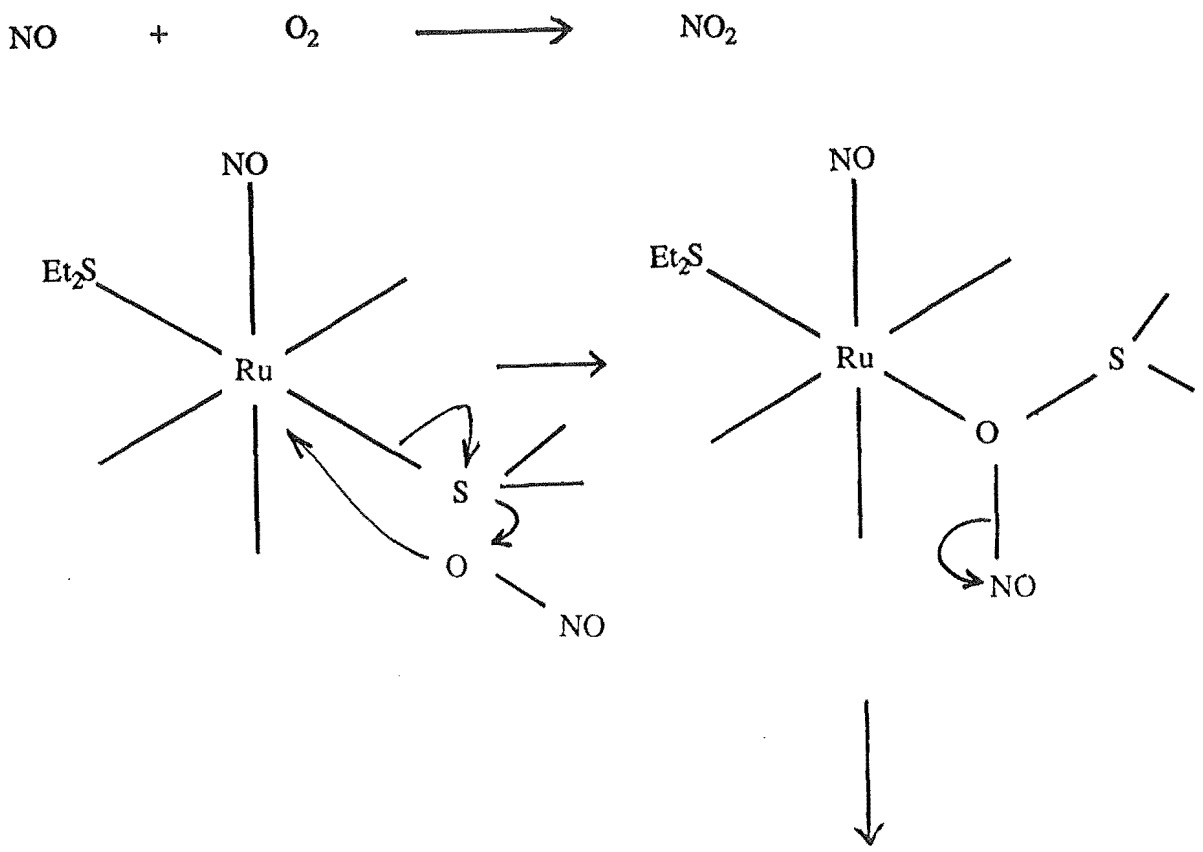
(A) Dissociative mechanism



SCHEME 3.6

Proposed mechanism for the formation of the organosulphide organosulphoxide complex $Ru(NO)X_3(Et_2S)(Et_2SO)$

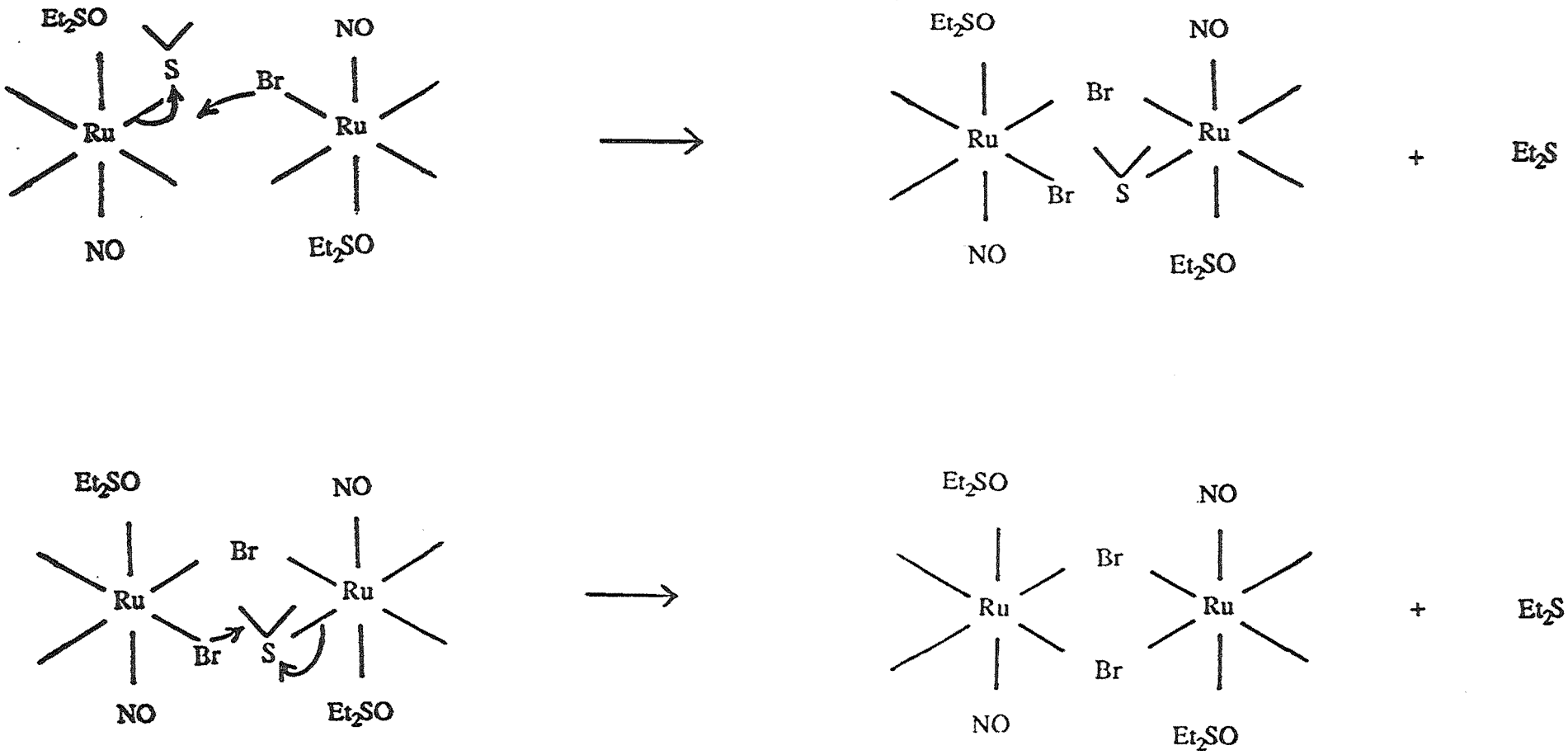
(B) Associative mechanism, attack by Et_2SO



SCHEME 3.6

Proposed mechanism for the formation of the organosulphide organosulphoxide complex $Ru(NO)X_3(Et_2S)(Et_2SO)$

(C) Associative mechanism, attack by NO_2



SCHEME 3.7

Proposed mechanism for the dimerisation step

3.6 THE FORMATION OF TRIBROMO(NITROSYL)-BIS(DIETHYLSULPHOXIDE)RUTHENIUM(II)

It is interesting that the final steps in the reaction involve the formation of the dimeric species $[Ru(NO)Br_3(Et_2SO)]_2$ and loss of R_2S (or R_2SO), and not the formation of a bis-diethylsulphoxide complex $Ru(NO)Br_3(Et_2SO)_2$. This complex was subsequently isolated by the reaction of very pure diethylsulphoxide with the '$Ru(NO)Br_3$' entity. However, meagre yields were obtained and only after numerous attempts. If there was even a small amount of Et_2S present (as an impurity) the diethylsulphide diethylsulphoxide complex was obtained. The elemental analytical results for the bis-sulphoxide complex are given in the experimental section at the end of this chapter.

The infrared spectrum for the bis-diethylsulphoxide complex is shown in Figure 3.4, and it is quite different to that of the diethylsulphide diethylsulphoxide complex, or the dimeric ruthenium complex. An interesting feature of the spectrum is the very strong absorbance at 920 cm^{-1}. This absorbance together with another strong absorbance at 1050 cm^{-1} suggests that the diethylsulphoxide ligands could be bound in two different modes, i.e. one sulphur bound and the other oxygen bound (see Chapter 2). However, some caution is necessary because an absorbance at 1050 cm^{-1} also occurs in the infrared spectrum of the bis-diethylsulphide complex.

The ^1H n.m.r. spectrum for the bis-diethylsulphoxide complex is shown in Figure 3.5. When the methyl group is decoupled the multiplet for the methylene protons collapses into four peaks. This suggests that the diethylsulphoxides are cis to each other as this would give rise to two peaks one for each of the inequivalent protons which would

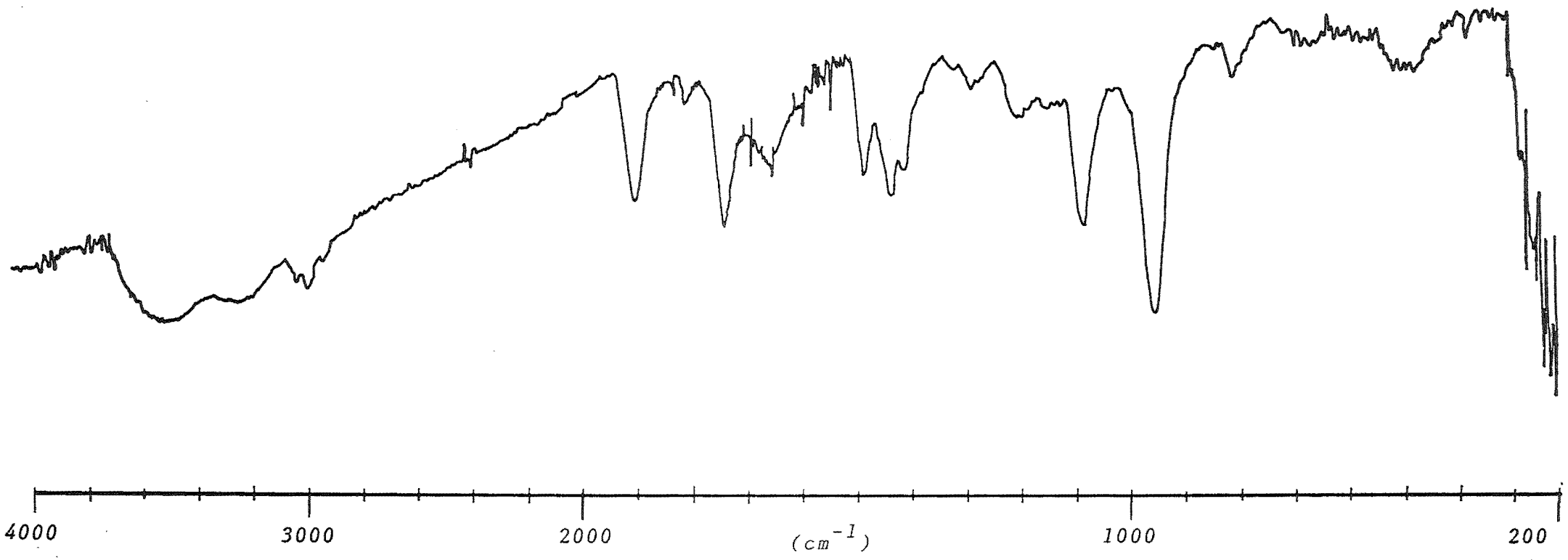
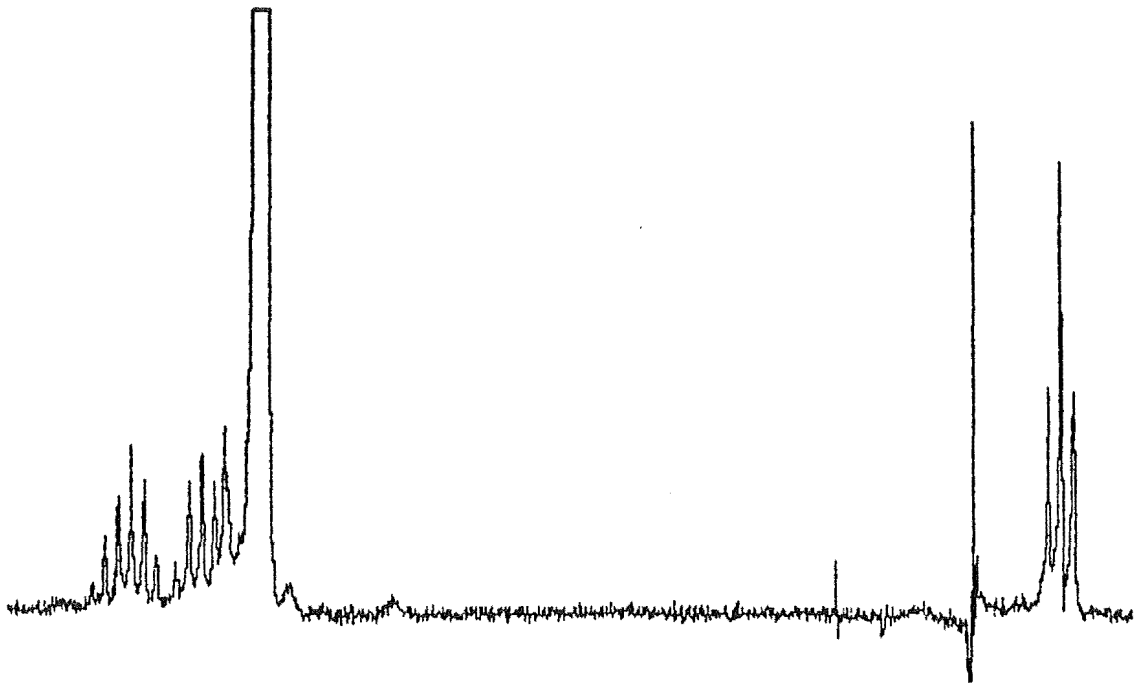
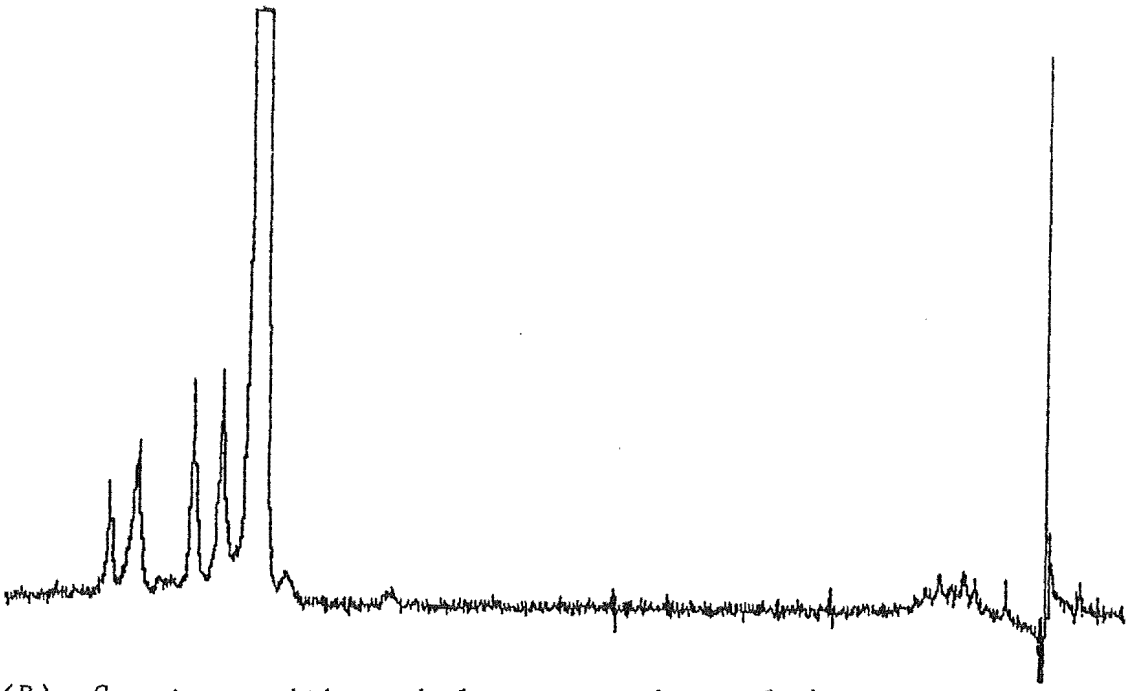


FIGURE 3.4

Infrared spectrum for $Ru(NO)Br_3(Et_2SO)_2$



(A) Undecoupled spectrum



(B) Spectrum with methyl protons decoupled

FIGURE 3.5

^{1}H *n.m.r. spectrum for* $Ru(NO)Br_3(Et_2SO)_2$

be split by the neighbouring proton. This assignment is supported by the ^{13}C n.m.r. spectrum which shows three resonances; δ = 6.6 ppm, 68.9 ppm and 43.8 ppm. The resonance at 6.6 ppm is likely to be due to the methyl carbon and the other peaks indicate that there are two furthur carbon magnetic environments. If the ligands are cis to each other there may be two different carbon resonances for the two different environments, one opposite the nitric oxide ligand, and one opposite a bromine atom. This suggests that in this complex one of the diethylsulphoxide ligands is opposite the nitric oxide ligand which is common for organosulphoxide nitrosyl complexes.

The X-ray powder diffraction pattern of the bis-diethylsulphoxide complex was measured and found to be quite different to any of the other diethylsulphoxide complexes studied in this work.

3.7 OTHER POSSIBLE MECHANISMS

3.7.1 Oxidation with Dioxygen as the Oxidising Agent

There are two other possible mechanisms that may be considered. In Scheme 3.8 (showing only the involvement of the sulphur containing ligands) dioxygen brings about the oxidation of the Et_2S ligand and a peroxy intermediate is formed. In the scheme the diethylsulphide and diethylsulphoxide ligands are shown in the trans arrangement, however as discussed above the stereochemical changes that are observed may occur in a number of ways. This scheme is similar to that proposed by Page (1978), but involves a second Et_2S ligand and a different method of hydrogen bonding assistance. For this scheme free radical scavengers would slow the reaction and the addition of some ethanol or

$$R_2S \xrightarrow{h\nu} R_2S^* \qquad \text{INITIATION}$$

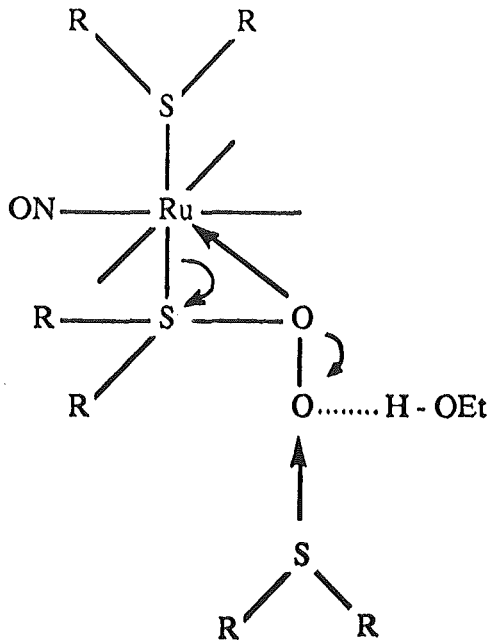
$$R_2S^* + O_2 \longrightarrow R_2SO^*_2 \qquad \left.\begin{matrix}\\\\\end{matrix}\right)$$

$$R_2SO^*_2 + R_2S \longrightarrow R_2SO_2 + R_2S^* \qquad \left.\begin{matrix}\\\\\end{matrix}\right) \text{PROPAGATION}$$

$$R_2SO_2 + R_2S^* \longrightarrow R_2SO + R_2SO \qquad \left.\begin{matrix}\\\\\end{matrix}\right)$$

$$R_2SO^*_2 + R_2SO \longrightarrow \text{OTHER PRODUCTS} \qquad \left.\begin{matrix}\\\\\end{matrix}\right) \text{TERMINATION}$$

HYDROGEN BONDING ASSISTANCE BY



SCHEME 3.8

An alternative mechanism for the photochemical reaction of $Ru(NO)Br_3(Et_2S)_2$ *with* O_2 *as the oxidising agent*

free diethylsulphide could assist the reaction by hydrogen bonding as indicated. This would reduce the electron density on the second oxygen atom and make it more susceptible to nucleophilic attack from the free diethylsulphide.

If loss of diethylsulphide occurs, then this step cannot be the rate determining step, and it is possible that a peroxy intermediate is formed while the sulphur atom is still bonded to the ruthenium atom. This scheme satisfies much of the experimental evidence. The reaction rate would increase on the addition of free ligand, ethanol, or other hydrogen bonding solvent and higher levels of dioxygen in solution. The reaction would be slowed down upon the addition of free radical scavengers and the oxidation of free organosulphides by dioxygen in the presence of UV radiation has been established (refer Section 3.3). However, the free ligand studies indicate that nitogen dioxide or a mixture of nitric oxide and dioxygen will oxidise the organosulphides more readily than dioxygen and UV radiation. The oxidation of the organosulphides was only readily achieved when they were dissolved in pure ethanol or methanol. The trace amounts of ethanol present in the chloroform were found to be insufficient to bring about this oxidation. However, the amount of ethanol present in chloroform may be sufficient for the amount of the ruthenium compound used in the photochemical reaction. Bubbling dioxygen through a solution of the complex whilst heating under reflux did not bring about any oxidation [Teow Sian Keong 1981], but it is possible that this step requires the dioxygen to be in an excited electronic state [Foote & Peters 1971; Correa & Riley 1985].

3.7.2 Oxidation with $RuBr_3(Et_2S)_3$ as the Oxidising Agent

A furthur proposal is outlined in Scheme 3.9. This involves loss of nitric oxide, and the formation of the complex tribromotris(diethylsulphide)ruthenium(III) $RuBr_3(Et_2S)_3$ which brings about the oxidation of the Et_2S ligand to Et_2SO.

This scheme also satisfies much of the experimental evidence and does require the loss of nitric oxide unlike Scheme 3.8. If this scheme is correct the oxidising agents are the tribromotris(diethylsulphide)ruthenium(III) complex and dioxygen, the latter required to regenerate the Ru(III) complex.

The oxidation of diethylsulphide in chloroform did occur when a solution containing $RuBr_3(Et_2S)_3$ and O_2 was irradiated. As this reaction proceeded the deep purple colour of the Ru(III) species was discharged, and the UV-visible spectrum of the reaction product was similar to that of a solution of the Ru(II) complex $Ru(NO)Br_3(Et_2S)_2$ dissolved in chloroform. This result supports the above scheme, and standard oxidation potentials predict that O_2 will bring about the oxidation of Ru(II) to Ru(III) with a driving force of +0.93 V under standard conditions. However, the free ligands studies showed that the oxidation of diethylsulphide is achieved much more readily with nitrogen oxides than with a $RuBr_3(Et_2S)_3/O_2$ mixture.

3.7.3 A Summary of the Proposed Mechanisms

In conclusion, whereas the mechanisms outlined in Schemes 3.8 and 3.9 satisfy much of the experimental data, they do not account for all of the observed facts. On the other hand the mechanism given in

$$Ru(NO)Br_3(Et_2S)_2 + h\nu \rightarrow Ru(NO)Br_3(Et_2S)_2^*$$

$$Ru(NO)Br_3(Et_2S)_2^* \underset{+Et_2S}{\overset{-NO}{\rightleftarrows}} RuBr_3(Et_2S)_3$$

$$Ru(NO)Br_3(Et_2S)_2 + RuBr_3(Et_2S)_3 \rightarrow$$
$$Ru(NO)Br_3(Et_2S^{\cdot})(Et_2S) + Ru(II)Br_3(Et_2S)_3$$

$$Ru(NO)Br_3(Et_2S^{\cdot})(Et_2S) + O_2 \rightarrow$$
$$Ru(NO)Br_3(Et_2SO_2^{\cdot})(Et_2S)$$

$$Ru(NO)Br_3(Et_2SO_2^{\cdot})(Et_2S) + Et_2S \rightarrow$$
$$Ru(NO)Br_3(Et_2SO)(Et_2S) + Et_2SO$$

$$Ru(II)Br_3(Et_2S)_3 + O_2 \rightarrow$$
$$Ru(III)Br_3(Et_2S)_3$$

SCHEME 3.9

An alternative mechanism for the photochemical reaction of $Ru(NO)Br_3(Et_2S)_2$ with $RuBr_3(Et_2S)_3$ as the oxidising agent

Scheme 3.4 explains all the known facts and is considered the most likely explanation.

PART B

THE PREPARATION AND PHOTOCHEMISTRY OF NITROSYL ORGANOCHALOCOGEN COMPLEXES OF RUTHENIUM(II)

3.8 THE PHOTOCHEMISTRY OF TRIHALOGENO(NITROSYL)-BIS(ORGANOSELENIDE)RUTHENIUM(II) COMPLEXES

$Ru(NO)X_3(RR'Se)_2$ X = Cl, Br; R = Et, R' = Et, Ph

3.8.1 The Photochemistry of Trihalogeno(nitrosyl)-bis(diethylselenide)ruthenium(II) Complexes

a) Introduction

The diethylselenide complexes $Ru(NO)X_3(Et_2Se)_2$ X = Br, Cl were investigated to see if they exhibited similar photochemical oxidation reactions to those found for the diethylsulphide complexes. Page (1979) had observed that diethylselenide complexes also underwent a colour change upon exposure to sunlight. A colour change was not observed in this study, but photochemical reactions did occur, and were followed using infrared and ^1H n.m.r. spectroscopy.

b) Stereochemistry of the complexes

The ^1H n.m.r. spectra for the starting materials were measured using a high field n.m.r. instrument and the fine splitting in the methylene resonance reported by Page using a 60 MHz instrument was now resolved.

The spectrum for the bromo- complex shown in Figure 3.6 has two separate regions for the methylene resonances; δ = 3.06, and 3.50 ppm. There are four quartets and this indicates that there is proton inequivalence. The methyl decoupled spectrum shows two doublets which would be due to the two different methylene environments (H_A and H_B) each split by the other methylene proton. Page (1978) and others [Cross et al. 1974; Abel et al. 1985] have shown that this inequivalence is due to inversion around the selenium, and occurs when the ligands are in the trans configuration. The inequivalence is more pronounced for the bromo- complex than the chloro- complex and is temperature dependent [Page 1978].

It is possible to re-interpret this spectrum as arising from a cis meridional isomer if ^{77}Se coupling occurs. Selenium coupling has been observed in the proton spectrum of other complexes [McFarlane & Wood 1972; Mila & Laurent 1967; Lardon 1970]. However, since the natural abundance and sensitivity are low, these spectra were reported to show small side bands due to selenium coupling rather than splitting of the main peaks [Lardon 1970]. No side bands were observed in the ^{1}H n.m.r. spectrum of the organoselenium complexes studied in this work.

That the complexes exist in the trans configuration is supported by the ^{13}C n.m.r. spectra which shows that there is only one resonance for the methylene carbon in both the bromo- and chloro- complexes δ = 27.9 ppm (bromo-), δ = 30.7 ppm (chloro-) [Fergusson & Page 1976]

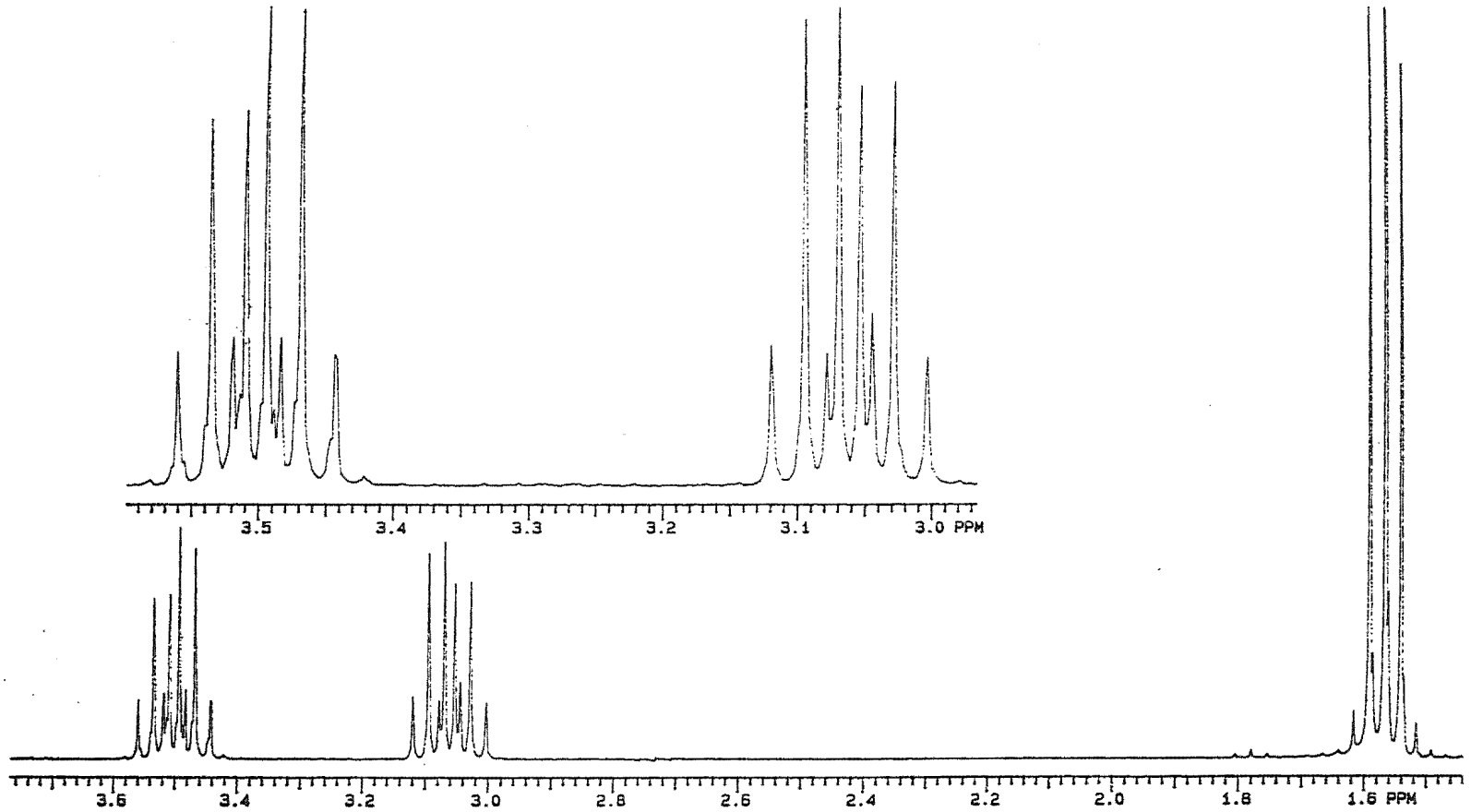


FIGURE 3.6

^{1}H *n.m.r. spectrum for* $Ru(NO)Br_3(Et_2Se)_2$

c) Oxidation of free organoselenides

Alkyl and arylselenides have been reported to undergo oxidation but this is achieved by ozone not dioxygen [Bagnall 1973]. Oxidation yields organoselenoxides and not organoselenones. Free dialkylselenoxides are somewhat unstable and decompose to give RSeH and RCHO. Diarylselenoxides also decompose yielding the diarylselenide and dioxygen. Alkylselenoxides have been obtained by oxidation of alkylselenides with nitrogen dioxide [Bagnall 1973; Paetzold et al. 1967] and addition compounds of the type $R_2SeO.N_2O_4$ have been reported. Free alkyl and arylselenoxides show an absorbance in their infrared spectra due to V(SeO) in the range 830 - 860 cm^{-1} [Ayrey et al. 1962].

d) Irradiation of the complexes

When the bromo- and chloro- diethylselenide complexes were intially studied they were exposed to sunlight for quite a long time (12 days) since the diethylsulphide analogues had required long exposure times before any reaction products were isolated. However, the infrared and ^1H n.m.r. spectra showed intense broad resonances and this suggested that substantial decomposition of the complexes had occurred. Hence the experiments were repeated using shorter exposure times (2 - 6 days).

After irradiation the solvent was removed under vacuum and the solid material analysed using infrared and ^1H n.m.r. spectroscopy. The infrared spectra of the products showed no apparent loss of NO and new strong broad absorbances at 700 - 750 cm^{-1} which is at a lower frequency than the V(SeO) stretching frequency for the free

organoselenoxides (830 - 860 cm^{-1}). The absence of a band at 830 - 860 cm^{-1} suggests that free organoselenoxide is not formed, but there may be some coordinated diethylselenoxide present. The ν(SeO) absorbance is likely to be shifted to a lower frequency when coordinated since this would lead to the build up of electron density in an orbital that was antibonding between the selenium and oxygen.

e) Interpretation of the ^1H n.m.r. spectra of the reaction products

The ^1H n.m.r. spectra of the irradiated complexes contained two new sharp resonances well separated from those of the starting material; a triplet at δ = 1.80 ppm and a quartet at δ = 3.89 ppm for the chloro- complex and a triplet at δ = 1.77 ppm and a quartet at δ = 3.83 ppm for the bromo- complex. Expansion of these peaks showed no evidence of further splitting and decoupling of these resonances showed that they were related to each other but not to any of the other resonances. There was also an increase in the complexity of the methylene region compared with the starting material. There were several overlapping multipets that were unable to be resolved and that were too close to each other to allow decoupling. There was evidence of new triplets close to the methyl resonance of the starting material for both the chloro- and bromo- complexes.

The resonances are not in the correct positions for any of the common ethyl groupings as found in ethanol, ethanoic acid, or diethylether and are not due to free diethylselenide [Hamada & Morishita 1977; Lazzeretti & Taddei 1971; Pouchert & Campbell 1974].

The ^{1}H n.m.r. spectrum for the bromo- complex is shown in Figure 3.7 and the interpretation of the spectrum in Figure 3.8. The increased complexity of the resonances in the methylene region is due to the appearence of new resonances which increase in size as the reaction proceeds and are accompanied by an increase of the absorbance at 700 - 750 cm^{-1} in the infrared spectrum.

If a diethylselenide diethylselenoxide complex is being formed, new resonances would be expected for the protons of the diethylselenide ligand and for the protons of the diethylselenoxide ligand. The resonances for the diethylselenide protons would be likely to occur in a similar region to those observed for the starting material whereas the resonanes for the diethylselenoxide ligand would be expected to occur at significantly different positions to that of the diethylselenide ligands.

f) Possible oxidising agents

In view of the reports in the literature of the oxidation of the free diethylselenide, it would seem likely that NO_2 is the oxidising agent rather than O_2. The mass spectrometer was unavailable to analyse the gaseous products so this suggestion remains speculative.

3.8.2 The Photochemistry of Trihalogeno(nitrosyl)-bis(ethylphenylselenide)ruthenium(II) Complexes

a) Introduction

The photochemical reactions of complexes of the stoichiometry $Ru(NO)X_3(EtSePh)_2$ for X = Cl, Br were also investigated using infrared

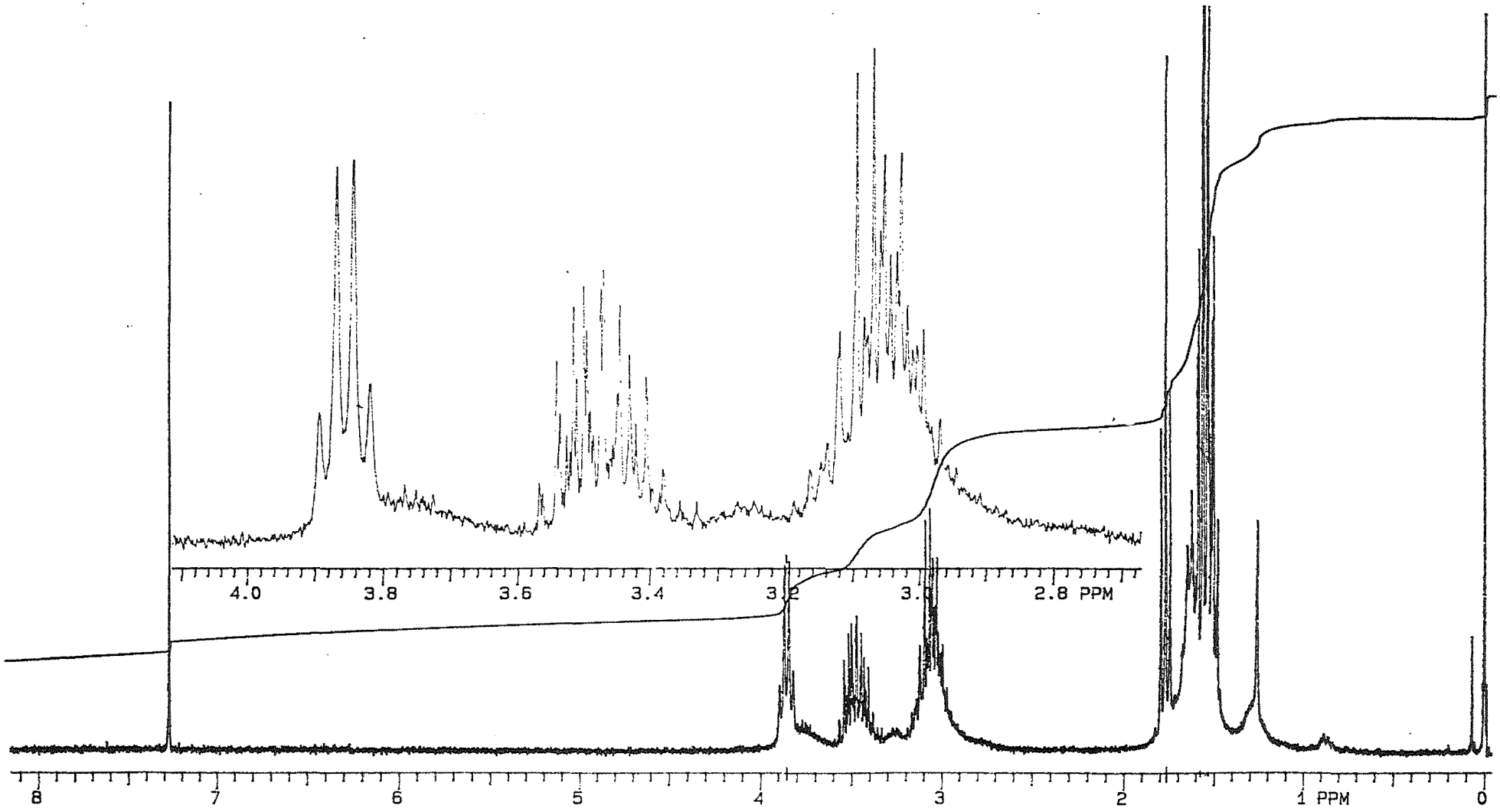
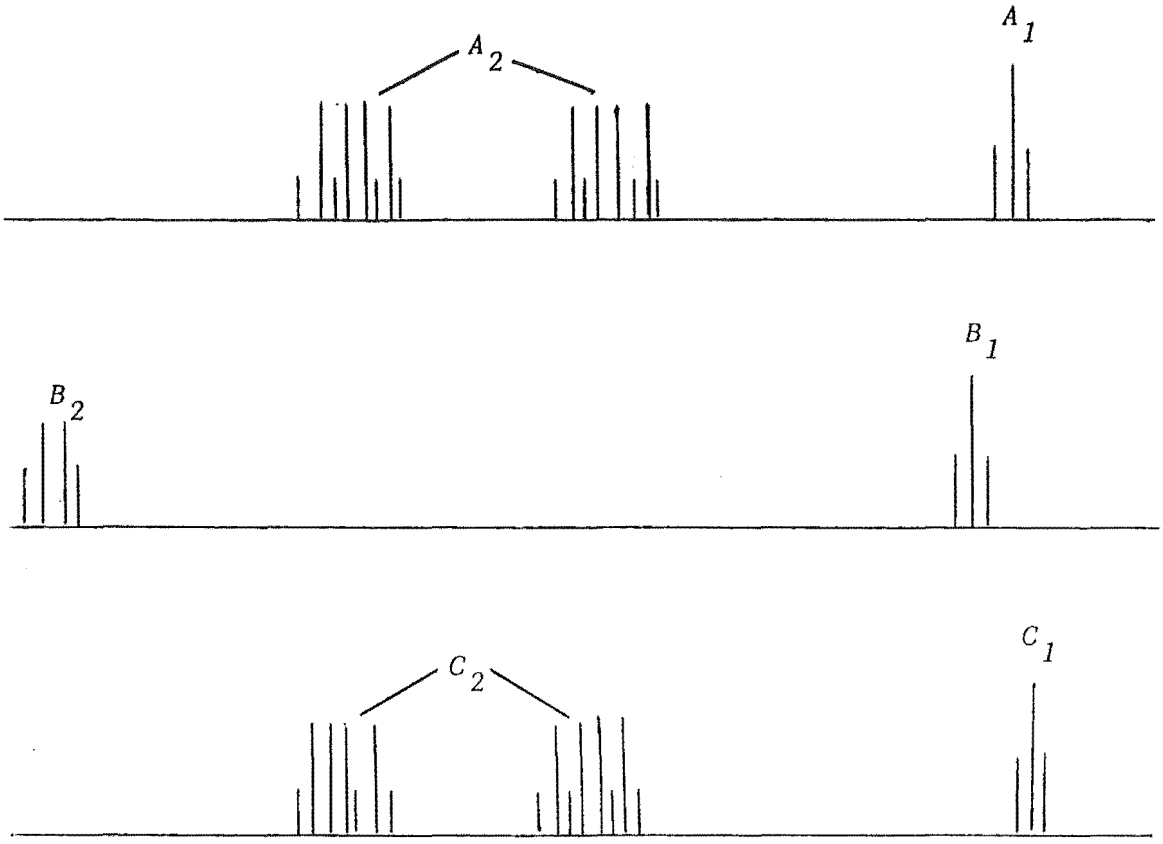
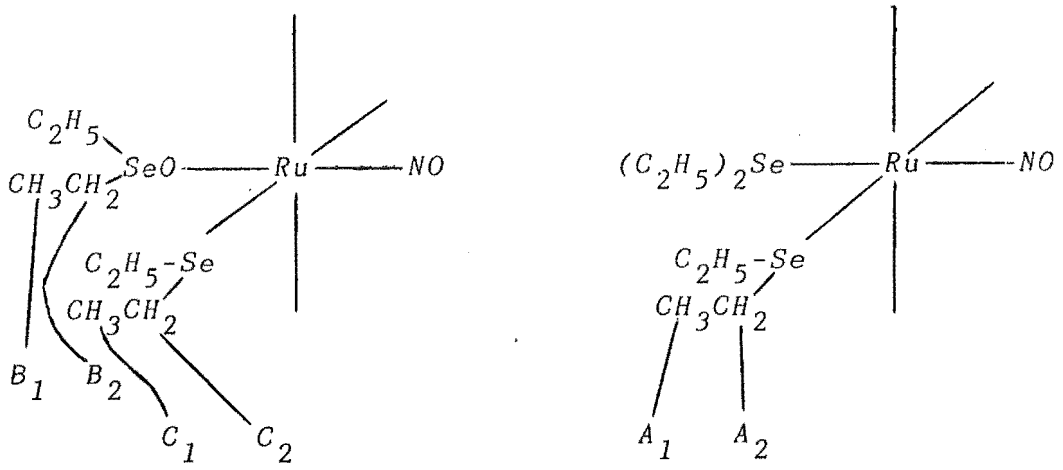


FIGURE 3.7

^{1}H *n.m.r. spectrum for* $Ru(NO)Br_3(Et_2Se)_2$ *after irradiation*





E 3.8

sed interpretation of the ^{1}H n.m.r. spectrum of
$)Br_3(Et_2Se)_2$ after irradiation

and ^{1}H n.m.r. spectroscopy. Like the diethylselenide complexes no colour change was observed upon irradiation.

b) Stereochemistry of the starting material

The ^{1}H n.m.r. spectra of the complexes were similar to that of the diethylselenide complexes in that there were two distinct regions for the methylene resonances indicating the presence of inequivalent methylene protons.

The methylene region was more complex than for the diethylselenide complexes. There was considerable overlap of the multiplets and it is difficult to be certain of the exact number of multiplets but there appears to be two sets of four quartets. The phenyl region showed two distinct resonances, δ = 7.41 ppm and 7.77 ppm due to the ortho and meta and para protons respectively. In the spectra there was some evidence for a splitting in the methyl resonance which may suggest that the methyl protons are not in equivalent magnetic environments. If this is the case then the complexes may exist (in solution at least) as the cis meridional isomer. This is surprising since one would expect the cis isomer to be less favoured due to the steric influence of the bulky phenyl groups. It is possible that there is some isomerisation occurring in solution but this would need to be rapid relative to the n.m.r. time scale.

The cis meridional configuration is supported by the ^{13}C n.m.r. spectra which show two magnetic environments for the methylene carbons for both the chloro- and bromo- complexes δ = 29.2, 29.5 ppm, (chloro-); δ = 31.0, 31.6 ppm (bromo-) [Fergusson & Page 1976].

c) Irradiation of the complexes

The complexes were irradiated and the solvent removed under vacuum. The solid products were studied using infrared and ^{1}H n.m.r. spectroscopy. Significant changes occurred in the ^{1}H n.m.r. spectra including the appearance of several board featurelss peaks. The methylene region became more complex, a new triplet appeared near the methyl resonance of the starting material, and there were new resonances in the phenyl region. For both complexes there was also a clear triplet (δ = 1.68 ppm) and quartet (δ = 3.44 ppm) separated from the other resonances as had been observed for the diethylselenide complexes, but these were less intense. The infrared spectra showed little change except for the development of a small broad absorbance at 880 cm^{-1} for both complexes.

These results suggest that a ethylphenylselenoxide complex may have been formed but the complexity of the ^{1}H n.m.r. spectra suggests that other products were also formed.

3.9 ATTEMPTS TO PREPARE TRIHALOGENO(THIONITROSYL)-BIS(DIALKYLSULPHIDE)RUTHENIUM COMPLEXES

Thionitrosyl complexes have been reported for many different transition metals including ruthenium [Roesky & Pandey 1984; Chivers & Edelmann 1986; Herberhold & Haumaier 1980]. Hursthouse et al. (1985) have disputed the identity of some of these complexes and suggest that some reported rhodium complexes containing thionitrosyl ligands [Pandey & Agarwala 1982; Pandey & Agarwala 1981; Pandey et al. 1981a; Pandey et al. 1980c] have to be confirmed.

Complexes of the form $M(NS)X_3L_2$ for L = R_3As, R_3P, M = Ru, Os are known [Roesky et al. 1984; Pandey & Agarwala 1980b; Bishop et al. 1975; Bishop et al. 1979] but no organosulphide complexes have been reported.

The trimeric compound trithiazl chloride $(NSCl)_3$ was used as the source of NS and was prepared from the reaction of thiodithiazl dichloroide $N_3S_2Cl_2$ with dichlorine [Jolly & Maguire 1967].

The preparation of thionitrosyl organosulphide complexes of ruthenium was attempted by reacting $(NSCl)_3$ with the following complexes; $Ru(NO)X_3(Et_2S)_2$ for X = Cl, Br, the dimer $[RuCl_3(Et_2S)_2]_2$, and a mixture of $RuCl_3 \cdot 3H_2O/Et_2S$. Different solvents were tried (THF and CH_2Cl_2) and a reaction carried out at room temperature and under reflux. No crystalline products were obtained after solvent removal, and the infrared spectra of the residues suggested that a complex mixture had been produced.

The complex $Ru(NS)Cl_3 \cdot xH_2O$ was made by the method of Bats et al. (1984) and reacted with Et_2S. In this case a crystalline product was obtained, but the analytical results were not consistent with an expected product $Ru(NS)Cl_3(Et_2S)_2$. Found: C = 49.1%, H = 3.33%; Calculated for $Ru(NS)Cl_3(Et_2S)_2$ [$C_8H_{20}Cl_3NS_3Ru$]; C = 22.2%, H = 4.6%.

The preparation of $Ru(NS)Cl_3(PPh_3)_2$ was carried out to check the reliabilty of the method and the reported product was obtained with an infrared spectrum similar to that reported. The product analysed with the correct stoichiometry. Found: C = 53.4%; H = 4.00%; N = 1.5%; Calculated for $Ru(NS)Cl_3(PPh_3)_2$ [$C_{36}H_{30}Cl_3NP_2SRu$]; C = 55.6%, H = 3.9%, N = 1.8%.

3.10 ATTEMPTS TO PREPARE NITRO COMPLEXES OF RUTHENIUM

3.10.1 Introduction

The investigation of the photochemical oxidation of $Ru(NO)X_3(R_2S)_2$ reported in the first part of this chapter has indicated that nitrogen dioxide may be the oxidising agent. Attempts were made to prepare a nitro complex of ruthenium to see if this complex would bring about the oxidation of the organosulphide ligands in the absence of dioxygen.

Nitro complexes of transition metals are known [Trogler & Marzilli 1974; Bhaduri et al. 1981; Seddon & Seddon 1984] but have not been reported for ruthenium organosulphide complexes.

Two methods were attempted; using very pure nitrogen dioxide, and using potassium nitrite as the nitrating agents.

3.10.2 Preparations Using NO_2

Pure NO_2 was prepared [Dodd & Robinson 1954] and passed through an ethanol solution of $RuCl_3.3H_2O/Et_2S$, at room temperature and under reflux. In another experiment pure NO_2 was passed through an ethanol solution of $RuCl_3.3H_2O$ and left overnight. The solvent was removed under vacuum and the residue taken up in fresh solvent and heated with Et_2S.

The infrared and ^1H n.m.r. spectra suggested that the reactions produced the bis(diethylsulphide) complex $Ru(NO)Cl_3(Et_2S)_2$ and in one case the mixed diethylsulphide diethylsulphoxide complex $Ru(NO)Cl_3(Et_2SO)(Et_2S)$ was obtained.

3.10.3 Preparations Using KNO_2

An ethanol solution of $RuCl_3.3H_2O$ and KNO_2 was heated under reflux and the solvent was removed under vacuum but there were no absorbances observed in the spectrum in the region expected for NO_2 and the ^1H n.m.r. spectrum was broad and featureless indicative of the presence of paramagnetic material.

3.11 EXPERIMENTAL

The elemental analytical results, infrared spectra, and ^{1}H n.m.r. spectra are summarised in Table 3.5 at the end of this section.

3.11.1 Preparation of the Ligands and Reagents

a) Organosulphides

Diethylsulphide was obtained commercially (Koch Light) and used without further purification. The other alkylsulphides were prepared as previously described [Mann & Purdie 1935] by heating under reflux the alkyl bromide (0.2 mol) in boiling ethanol with anhydrous sodium sulphide (0.2 mol), evaporation of the solvent and washing with water, followed by extraction with diethylether. The alkyl-arylsulphides were prepared similarily [Ipatieff et. al. 1938] using thiophenol. The products were purified by ordinary distillation.

b) Diethylsulphoxide and diethylsulphone

Diethylsulphoxide was prepared by two different methods, both involving the oxidation of diethylsulphide. The first method [Johnson & Keiser 1966] involved oxidation of the diethylsulphide (9.0ml) at low temperature (ca. -5.0 ^{o}C) by addition of diethylsulphide to a solution of 22.5g of sodium periodate and stirring for 16 hours. This method produced a mixture of diethylsulphoxide and diethylsulphone which was separated using a BUCH GKR 50 rotorvap. The second method [Harville & Reed 1968] involved oxidation of 18g (0.2mol) of diethylsulphide in anhydrous methanol, by the addition of 35.958g

(0.2mol) of N-bromosuccinamide in 5g increments at such a rate to keep the temperature less than 10 ^{o}C. After the addition was complete the solution was allowed to warm to room temperature and stand for an hour. The solvent was removed and the diethylsulphoxide extracted with diethylether from the resulting liquid solid residue. The diethylsulphoxide was purified by distillation under vacuum. Yields of diethylsulphoxide by the latter method were higher and the product more pure.

c) Nitric oxide

Nitric oxide was conveniently prepared by the addition of dilute (2M) sulphuric acid dropwise to powered sodium nitrite under dinitrogen [Schenk 1963]. Several other methods were also attempted involving heating of pellets made from nitrite [Ray & Ogg 1956; Beattie 1967a] and addition of acid onto a mixture of potassium nitrite and potassium iodide but all with less success.

When the gas was required pure it was passed through two traps containing 10M alkali, a drying tube with pelletised sodium hyroxide, and three cold traps (dry ice/ethanol) to trap any nitrogen dioxide [Feltham & Carriel 1964; Feltham 1964].

Pure nitric oxide is a colourless solid that melts at -163.6 ^{o}C to give a deep blue liquid which boils at -151.8 ^{o}C to give a colourless gas.

d) Nitrogen dioxide

Nitrogen dioxide was prepared by mixing nitric oxide made as described above with an excess of dioxygen [Dodd & Robinson 1954] and

purifying by slow distillation through a series of cold traps at -105 ^{o}C (ethanol/liquid N_2). The nitrogen dioxide was collected in a trap while flushing with pure dioxygen and then allowed to distil over slowly into the next trap under a slow flow of dioxygen. The nitric oxide thus was converted into nitrogen dioxide and collected. Any unreacted nitric oxide passed through the trap as its boiling point (-163.6 ^{o}C) was too low for it to be trapped.

Preparations via thermal decomposition of dinitrogenpentoxide [Hackspill & Besson 1949; Daniels & Bright 1920; Gruenhut et. al. 1950; Caesar & Goldfrank 1946; Beattie 1967b; Pedar & Pollard 1957; Addison & Logan 1973; Beattie 1967c] were also attempted but were unsuccessful.

Pure nitrogen dioxide is a colourless solid which melts at -11.2 ^{o}C to give a yellow liquid which boils at 21.2 ^{o}C to give a brown gas.

e) Dioxygen free dinitrogen

Dioxygen was removed from dinitrogen by passing commercially available dioxygen free dinitrogen through a BTS catalytic dioxygen scrubber (BASF) or using an ammonium vanadate oxygen scrubber. The BTS catalytic dioxygen scrubber consists of finely divided copper on a carrier. The catalyst was heated (110 ^{o}C) and the Cu reacted with any O_2 to form CuO.

The ammonium vanadate oxygen scrubber was prepared by dissolving $VOSO_4.2H_2O$ (0.45g) in 50ml of 2M H_2SO_4 and placing this solution in a gas bubbler over a Zn/Hg amalgam. The Zn/Hg amalgam was prepared by stirring 50g of granulated zinc in a 2% solution of $HgCl_2$ until the surface of the zinc became coated with mercury. The excess $HgCl_2$ was

removed by repeated washing with distilled water. When the vanadium solution was added to the Zn/Hg amalgam the solution changed colour from blue to green to violet showing the changes in oxidation state of the vanadium from V(IV) to V(III) to V(II) as it was reduced.

f) Thiodithiazl dichloride $S_3N_2Cl_2$

The method of Jolly & Maguire (1967) was used on a reduced scale. Ammonium chloride (100g), sulphur (20g), and disulphurdichloride S_2Cl_2 (100ml) were heated under reflux in a specially made 500ml round bottomed flask. A 500 mm air condenser was fitted to the flask and a drying tube containing anhydrous calcium chloride connected to the top of the air condenser. As the reaction proceeded the $S_3N_3Cl_2$ formed as light orange crystals in the lower part of the air condenser and the round bottomed flask was made with a specially shortened neck so that the crystals formed in the condenser rather than inside the flask. The mixture was heated under reflux for 12 - 16 hours. All the glassware had been predried overnight in an oven at 100 ^{o}C. The product was not isolated was but reacted with Cl_2 to prepare $(SNCl)_3$.

g) Trithiazl chloride $(SNCl)_3$

Thiodithiazl dichloride prepared above was treated with Cl_2 as described by Jolly & Maguire (1967). The round bottomed flask was removed and quickly stoppered. The top of the air condenser was connected to a vacuum line and the $S_3N_3Cl_2$ thoroughly evacuated for 30 minutes. The transfer of the air condenser to the vacuum line needs to be preformed quickly because the thiodithiazl dichloride is very sensitive to moisture or dioxygen. After evacuation the stopper

was replaced with a three necked round bottomed flask and the top of the air condenser fitted with a drying tube containing anhydrous calcium chloride. Dichlorine gas from a small cylinder (Matheson) was passed through the air condenser. A dark brown liquid formed which flowed into the flask. After treatment with Cl_2 for 30 minutes, the drying tube was replaced with a stopper and the whole system evacuated for 30 minutes. This removed the volatile sulphur(II)chloride and the $(SNCl)_3$ remained as a pale yellow solid. Chlorination was judged complete after a further two treatments with Cl_2 when no further darkening of the material occurred. The whole apparatus was fitted with drying tubes and quickly transferred into a dry box and the flakey crystals of $(SNCl)_3$ removed and stored in the dark in a desiccator over phosphorus pentoxide.

h) Anhydrous sodium sulphide

Commercial hydrated sodium sulphide was powdered and left in a vacuum desiccator under high vacuum over concentrated sulphuric acid for two weeks. After this time the pale yellow colour faded and a white powder remained [Feher 1963].

i) MNTS N-methyl N-nitroso p-toluenesulphonamide

MNTS was obtained commercially (Aldrich) and used without further purification. Attempts to recrystallise an old sample of MNTS from benzene [Perrin et al. 1980] were unsuccessful.

3.11.2 Purification of Solvents

The solvents were purified as described by Perrin et al.(1980).

a) Ethanol free chloroform

Chloroform (200ml) was treated with concentrated sulphuric acid (20ml) and then washed thoroughly with water, dried over anhydrous calcium chloride and then distilled.

b) N_2, O_2 and Ar saturated chloroform

Chloroform was heated under reflux for 30 minutes and allowed to cool under an atmosphere of O_2, N_2, or Ar (from a cylinder) by bubbling the gas through a fritted gas bubbler until the solvent cooled to room temperature. These solutions were not stored but made up freshly each time just prior to being used in an experiment. The N_2 used was made O_2 free as described in above.

c) Pyridine

Pyridine was dried by standing over potassium hydroxide pellets for 48 hours followed by distillation.

d) Petroleum ether

Petroleum ether was dried by heating under reflux with $LiAlH_4$ for a minimum of one hour and then distilling.

e) Tetrahydrofuran

Tetrahydrofuran was dried in the same way as for petroleum ether.

f) Dichloromethane

Dichloromethane was dried by heating under reflux over anhydrous calcium chloride and distilling.

g) Diethylether

Diethylether was dried by heating under reflux with $LiAlH_4$ and distilling.

3.11.3 Preparation of the Complexes

a) Trihalogeno(nitrosyl)bis(organochalcogen)ruthenium(II)

$Ru(NO)X_3(R_2E)_2$ for X = Br, Cl; E = S, Se

The '$Ru(NO)Cl_3$' entity was produced by bubbling nitric oxide gas through an ethanol solution (1.0g in 100ml) of commercial $RuCl_3 \cdot 3H_2O$ for 3-4 hours, and leaving the nitric oxide saturated solution overnight. A portion of this solution (30ml containing approx. 0.3g of $RuCl_3 \cdot 3H_2O$) was heated under reflux with Et_2S (0.5g) in ethanol (10ml) for 90 minutes and the volume of solution reduced under vacuum until crystallisation occurred. Preparations using anhydrous $RuCl_3$ were unsuccessful resulting in meagre yields or no crystalline products.

The bromo- analogue was obtained by evaporating the '$Ru(NO)Cl_3$' entity to dryness on a water bath several times in a small amount

(10-15ml) of pure 4M HBr. If the complex was allowed to heat for any length of time after evaporation has been completed or was heated too stongly (for example on a hot plate) some form of thermal decomposition occurred and the resulting residue was insoluble in ethanol resulting in a substantially reduced yield of the complex.

Attempts were made to prepare the iodo- complex as outlined by Page (1978) and Teow Sian Keong (1981). The chloro- complex was heated under reflux with HI (1g in 30ml of ethanol) for 6 hours in ethanol, evaporated to dryness and washed with dichloromethane to remove iodine but no crystalline product was obtained. Metathetical replacment was also attempted by heating under reflux the chloro- complex for two hours with NaI (10:1 excess) followed by removal of the solvent under vacuum. Different solvents were tried (ethanol and 2-methoxyethanol) but elemental analysis of the crystalline product obtained indicated that the halogen replacement was incomplete. Found: C = 21.4%, H = 4.9%; Calculated for $Ru(NO)I_3(Et_2S)_2$ $[C_8H_{20}I_3NOS_2Ru]$; C = 13.9%, H = 2.9%.

The chloro- complex $Ru(NO)Cl_3(Et_2S)_2$ forms orange crystals and the bromo- complex $Ru(NO)Br_3(Et_2S)_2$ forms dark brown crystals.

The preparation of the complex $Ru(NO)Cl_3(Et_2S)_2$ was also attempted using MNTS. The complex $RuCl_3 \cdot 3H_2O$ (0.13g) in ethanol (20ml), and MNTS (0.2g) in ethanol (10ml), were added quickly and successively to a boiling solution of diethylsulphide (0.5g) in ethanol (40ml) and heated under reflux for 15 minutes. The solvent was removed under vacuum to produce a brown powder but there was no evidence for coordinated nitric oxide in the infrared spectrum of the product.

The above method provides a general route for the synthesis of trihalogeno(nitrosyl)bis(organochalcogen)ruthenium(II) complexes.

b) Trihalogenotris(diethylsulphide)ruthenium(III)

$RuX_3(Et_2S)_3$ for X = Cl, Br.

Hydrated trichlororuthenium(III) $RuCl_3.3H_2O$ (0.25g) and diethylsulphide (0.9g) were heated under reflux in ethanol (30ml) for 1 hour and the solvent evaporated under vacuum [Fergusson et. al. 1965]. Black crystals of the dimeric complex di-μ-chlorobis[dichlorobis(diethylsulphide)ruthenium(III)] $[RuCl_3(Et_2S)_2]_2$ separated out intially. Further evaporation yielded bright orange crystals of the desired complex. The bromo- analogue was made by metathetical replacement by adding a 10:1 ratio of KBr (1g) to 0.5g of the chloro- complex in 50ml of ethanol and heating under reflux for 30 minutes.

c) Di-μ-chlorobis[dichlorobis(diethylsulphide)-ruthenium(III)] $[RuCl_3(Et_2S)_2]_2$

The black dimeric complex $[RuCl_3(Et_2S)_2]_2$ was obtained during the preparation of trichlorotris(diethylsulphide)ruthenium(III) as outlined in (b) above.

d) Tribromo(nitrosyl)bis(diethylsulphoxide)ruthenium(II)

$Ru(NO)Br_3(Et_2SO)_2$

The complex $Ru(NO)Br_3(Et_2SO)_2$ was prepared in a similar manner as the bis-diethylsulphide complexes by the addition of highly pure

diethylsulphoxide (0.5ml) to a boiling solution of the '$RuNOBr_3$' entity (made form 0.3g of $RuCl_3.3H_2O$) in ethanol (30ml) and heating under reflux for 30 minutes. The solution was placed in a small beaker and the solvent was allowed to evaporate off slowly at low temperature (ca. 4 ^oC) yielding a small quantity (yield < 10%) of a dark brown precipitate.

e) Dichlorotris(triphenylphosphine)ruthenium(II)

$RuCl_2(PPh_3)_3$

This complex was prepared by the method of Stephenson & Wilkinson (1966). The complex $RuCl_3.3H_2O$ (0.2g) was heated under reflux with PPh_3 (1.2g) in methanol in a dinitrogen atmosphere for 2 hours. The solvent was removed under vacuum and brown micro crystals precipitated which were washed with methanol and diethylether and dried under vacuum.

f) Trichloro(thionitrosyl)ruthenium(II) hydrate

$Ru(NS)Cl_3.xH_2O$

The complex $Ru(NS)Cl_3.xH_2O$ was prepared by the method of Bats et. al. (1984). Trithiazl chloride $(SNCl)_3$ (2.69g) was dissolved in fresh dry tetrahyrofuran (30ml) and added dropwise to the complex $RuCl_3.3H_2O$ (2.69g) dissolved in fresh dry tetrahydrofuran (100ml) under an atmosphere of dioxygen free dinitrogen. This solution was stirred at room temperature for five hours and a dark brown powder separated out that was collected and thoroughly washed with methanol. The yield was quantitative and the product showed an absorbance in the infrared

spectrum at 1400 cm^{-1} assigned to ,(NS) as reported. There was also evidence in the infrared spectrum for coordinated H_2O.

The complex is dark brown, soluble in water and moderately soluble in 2-methoxyethanol, but insoluble in chloroform, ethanol, methanol, and dichloromethane.

g) Organoselenide complexes

The complexes $Ru(NO)X_3(Et_2Se)_2$ and $Ru(NO)X_3(EtSePh)_2$ for X = Cl, Br were available from previous studies in the department. These complexes can be prepared by a method similar to that used to make the bis-organosulphide complexes described above [Page 1978].

3.11.4 Experimental Conditions for the Reaction of the Ligands with Gases and the Photochemical Reactions

a) Photochemical reaction of the ligands

The ligand (1ml) was dissolved in solvent grade chloroform (50ml) and placed 200 mm in front of a mercury discharge lamp for varying lengths of time (30 minutes to 120 minutes). These reactions were carried out in a 250ml three necked round bottom quartz flask. When gases such as nitric oxide or dioxygen or nitrogen dioxide were bubbled through the solutions, a condenser was fitted to reduce the loss of chloroform by evaporation. The gases were passed through the solutions and at the conclusion of the experiment the solvent was removed under vacuum and the reaction products analysed using n.m.r. or infrared spectroscopy. In the cases in which the solution was heated, an infrared lamp was used as the heat source.

b) Reaction of ligands with NO/O_2 and NO_2

The experiment was carried out in a blackened flask fitted with a blackened condenser and stoppers. The ligand (1ml) was dissolved in the chloroform (50ml) and the gas bubbled through a fritted gas bubbler (10 - 30 minutes). The solvent was removed under vacuum and the reaction products analysed using n.m.r. or infrared spectroscopy.

c) Photochemical reactions of the organosulphide complexes.

The complex (0.18g) was dissolved in solvent grade chloroform (saturated with O_2 or N_2) and placed in a quartz tube (20 mm ID x 120 mm long) that was fitted with a teflon vacuum tap and a B14 ground-glass joint. The quartz tubes (at this stage covered with aluminium foil to prevent reaction occurring prematurely) were frozen with liquid nitrogen attached to a vacuum line and thoroughly evacuated for 30 minutes under a high vacuum using an oil diffusion pump. The reaction mixture was allowed to thaw and was irradiated with a mercury lamp at a distance of 200 mm for varying lengths of time and the gas evolved analysed using a SMS DATAQUAD or AEI MS 902 mass spectrometer. For the measurements using the SMS DATAQUAD the tubes were attached to the gas handling section of the mass spectrometer and the portion of the tube above the tap evacuated for 15 minutes and then 15 mm of mercury of gas admitted into the glassware. This gas was then sampled and analysed. For the blank samples (containing only chloroform) and the reaction mixture, the total backgrounds of the gas remaining in the mass spectrometer and in the gas handling glassware were recorded and stored by the

microprocessor and then subtracted from the measured spectrum. The solid products were analysed by n.m.r. and infrared spectroscopy after solvent removal under vacuum. When the AEI MS 902 was used the solutions were allowed to thaw and the portion of the tube above the tap evacuated. The solutions were refrozen in an EtOH/liquid N_2 slush bath at ca. -105 ^{o}C before letting the sample into the mass spectrometer. It was necessary to refreeze the solution before sampling the gaseous mixture because the AEI MS 902 gas inlet system would have sucked some of the chloroform up into the mass spectrometer because of the high vacuum present.

d) Photochemical reactions of the organoselenide complexes

The complex (0.05g) was dissolved in reagent grade chloroform (20ml) in a test tube and placed in direct sunlight for up to 12 days.

Compound	^{1}H n.m.r. (ppm)	Infrared cm^{-1}	Elemental anal. C, H Found(calculated)
Et_2S	1.27(T), 2.57(Q)		
Et_2SO	1.33(T), 2.70(Q)	1055 ν(SO)	
Et_2SO_2	1.40(T), 2.97(Q)		
$Ru(NO)Cl_3(Et_2S)_2$	1.48(T), 3.20(Q)	1850 ν(NO)	22.9(23.0), 4.7(4.8)
$Ru(NO)Br_3(Et_2S)_2$	1.50(T), 3.28(Q)	1860 ν(NO)	17.6(17.4), 4.0(3.7)
$RuCl_3(Et_2S)_3$			29.0(30.1), 6.5(6.3)
$RuBr_3(Et_2S)_3$			22.8(23.6), 4.7(4.9)
$Ru(NO)Br_3(Et_2SO)_2$	2.69(Q), 2.75(Q) 2.83(Q), 2.87(Q)	1875 ν(NO) 930 ν(SO)	16.7(16.5), 3.2(3.5)
$Ru(NS)Cl_3.xH_2O$		1400 ν(NS)	
$Ru(NS)Cl_3(PPh_3)_2$		1320 ν(NS)	53.4(55.6), 4.0(3.9)
$RuCl_2(PPh_3)_3$			67.1(67.6), 5.1(4.7)

KEY

S = singlet T = triplet Q = quartet

TABLE 3.5

Summary of the elemental analytical results and spectral data for ligands and complexes studied.

CHAPTER 4

THE PREPARATION AND PHOTOCHEMISTRY OF RUTHENIUM AND OSMIUM NITROSYL COMPLEXES

4.1 INTRODUCTION

In this chapter the preparation and photochemistry of nitrosyl complexes of the stoichiometric type $M(NO)X_3L_2$ for M = Os, Ru; X = Br, Cl; L = PPh_3, Et_2PPh is described. The chapter is divided into two parts. In Part A the photochemistry of trihalogeno(nitrosyl)-bis(organophosphine)ruthenium(II) complexes is described, and in Part B the photochemistry of trihalogeno(nitrosyl)bis(organophosphine)-osmium(II) complexes is given. The preparation of some trihalogeno(nitrosyl)bis(organosulphide)osmium(II) complexes was also investigated and is described in Part B.

PART A

THE PHOTOCHEMISTRY OF SOME TRIHALOGENO(NITROSYL)-BIS(ORGANOPHOSPHINE)RUTHENIUM(II) COMPLEXES

4.2 THE PHOTOCHEMISTRY OF TRIHALOGENO(NITROSYL)-BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II) COMPLEXES

$Ru(NO)X_3(PPh_3)_2$ for X = Cl, Br

4.2.1 Introduction

The oxidation of organophosphines has been extensively studied and there have been a number of reports of the oxidation of free

organophosphines to the organophosphineoxides by nitrogen oxides. In many of these studies it has been reported that nitric oxide will achieve the oxidation and nitrogen dioxide is not required in contrast to what has been found for organosulphides [Longhi et al. 1962; Halmann & Kugel 1962; Kuhn et al. 1960; Hieber & Karamolowsky 1963; Addison & Sheldon 1956; Banks et al. 1968]. The principal reaction products were the organophosphineoxide and dinitrogenoxide. Organophosphines may also be oxidised by dioxygen, alkylphosphines require heating, but arylphosphines require UV radiation [Geoffroy et al. 1976b; Buckler 1962]. The rate of oxidation of free organophosphines by dioxygen in the presence of UV radiation is increased when ruthenium or other transition metal complexes are present. The complexes used are often five coordinate and contain organophosphine ligands [Cenini et al. 1972; Taqui-Khan et al. 1971; Graham et al. 1972; Graham et al. 1970; Rossi & Sacco 1971]. Platinum metal complexes with coordinated dioxygen assist in the oxidation of organophosphines [Wilke et al. 1967; Sen & Halpern 1977; Marmion & Takeuchi 1986; Laing & Roper 1968a], and ruthenium dioxygen complexes have been reported to catalyse the oxidation of organophosphines [Graham et al. 1972; Graham et al. 1970; Riley & Shumate 1984]. Oxidation of free organophosphines by oxygen atom transfer from a transition metal nitrosyl complex has been reported [Rossi & Sacco 1971; Doughty et al. 1981; Solar et al. 1985; Tovrog et al. 1979] and is said to involve the formation of an intermediate bis-nitrosyl complex.

Oxidation of a coordinated organophosphine ligand has been reported using dioxygen and UV radiation [Udupa et al. 1983]. Oxidation of triphenylphosphine to the oxide by a complex that

contained both nitric oxide and dioxygen has been reported [Graham et al. 1970]. The complex $Ru(O_2)(NO)(NCS)(PPh_3)_2$ is an efficient homogenous catalyst for the oxidation by free dioxygen of triphenylphosphine to the oxide. The nitric oxide does not appear to be involved in the oxidation, except in its ability to alter from a three electron to a one electron donor (Chapter 2). This change allows triphenylphosphine to form an intermediate six coordinate complex $Ru(O_2)(NCS)(NO)(PPh_3)_3$.

4.2.2 Free Ligand Studies

The oxidation of triphenylphosphine by various oxidising agents was investigated. Triphenylphosphine was readily oxidised by nitrogen dioxide and it was confirmed that nitric oxide would also bring about the oxidation in reagent grade chloroform. Comparison of the rate of the above oxidation with that achieved using dioxygen and UV radiation indicated that the nitric oxide was more effective. Triphenylphosphineoxide was identified from its ^1H n.m.r. spectrum, where a downfield shift occurred in the position of the complex phenyl resonance from δ = 7.35 ppm for PPh_3 to 7.62 ppm for $OPPh_3$ [Pouchert & Campbell 1974]. The infrared spectrum of $OPPh_3$ had absorbances at 1120 cm^{-1} and 1180 cm^{-1} ppm which compared well with reported values [Bellamy 1975; Hudson 1965; Thomas & Chittenden 1961; Thomas & Chittenden 1964; Geoffroy et al. 1976b; Kukushkin & Sedova 1980].

4.2.3 The Photochemical Reaction

The complexes $Ru(NO)Cl_3(PPh_3)_2$ and $Ru(NO)Br_3(PPh_3)_2$ were low in solubilty. However, when chloroform suspensions of the complexes were

irradiated with sunlight a small quantity appeared to dissolve forming a pale brown solution. The solvent was removed under vacuum and the infrared spectra measured for the solid products. The low solubility of the chloro- and bromo- products precluded any n.m.r. studies and therefore the evidence for reaction is based on the infrared spectra, elemental analytical results, and the mass spectrometric results for the bromo- complex.

4.2.4 Mass Spectrometric Studies of the Photochemical Reaction of Tribromo(nitrosyl)bis(triphenylphosphine)ruthenium(II)

A mass spectrometric analysis of the gaseous products of the reaction of free triphenylphosphine with nitric oxide showed an increase in the peak at mass 44 and a reduction in the peak at mass 30. From this it is suggested that the nitric oxide oxidised the triphenylphosphine and was reduced to dinitrogenoxide as illustrated below;

$$2NO + PPh_3 \rightarrow N_2O + OPPh_3$$

mass 30 mass 44

The gaseous products of the irradiation of $Ru(NO)Br_3(PPh_3)_2$ in chloroform showed an increase for the peak at mass 44 and mass 30. When the chloroform was made dioxygen free the increase at mass 44 was still observed. The addition of free ligand (triphenylphosphine) to the reaction mixture inhibited the loss of the nitric oxide, in contrast to the organosulphides. The increase in the peak at mass 30

detected when the complex $Ru(NO)Br_3(PPh_3)_2$ was irradiated was less than than that seen for the organosulphide complexes $Ru(NO)X_3(Et_2S)_2$, but this may be due to the much lower solubility of the triphenylphosphine complexes in chloroform.

A high resolution mass spectrometric analysis, using the AEI MS 902, established that the increase in the peak at mass 44 was due to dinitrogenoxide. Found: Mass = 44.001045; Calculated for N_2O = 44.001060; Calculated for CO_2 = 43.989852.

4.2.5 Discussion

The infrared spectrum for the chloro- complex is shown in Figure 4.1. and after irradiation in Figure 4.2. The absorbance at 1120 cm^{-1} in Figure 4.2 may be assigned to V(PO), and an absorbance at 540 cm^{-1} to V(Ru-O) [Kukushkin et al. 1981]. A third strong absorbance at 720 cm^{-1} may be assigned to a bending mode of the phosphorus-oxgyen linkage. The presence of the latter two absorbances are indicative of coordinated triphenylphosphineoxide. The absorbance at 540 cm^{-1} sometimes appears as a shoulder on an adjacent peak. There is no evidence for an absorbance at 1180 cm^{-1} which occurs for uncoordinated triphenylphosphineoxide [Geoffroy et al. 1976b]. The solid chloro- and bromo- products analysed well for the stoichiometry $Ru(NO)X_3(OPPh_3)(PPh_3)$. Found: C = 55.6%, H = 4.6%; Calculated for $Ru(NO)Cl_3(OPPh_3)(PPh_3)$ $[C_{36}H_{30}Cl_3NO_2P_2Ru]$; C = 55.6%, H = 3.9%. Found: C = 47.6%, H = 4.1%; Calculated for $Ru(NO)Br_3(OPPh_3)(PPh_3)$ $[C_{36}H_{30}Br_3NO_2P_2Ru]$; C = 47.4%, H = 3.3%.

The most likely oxidising agent is nitric oxide and this is suggested by the presence of N_2O in the mass spectrum of the gaseous

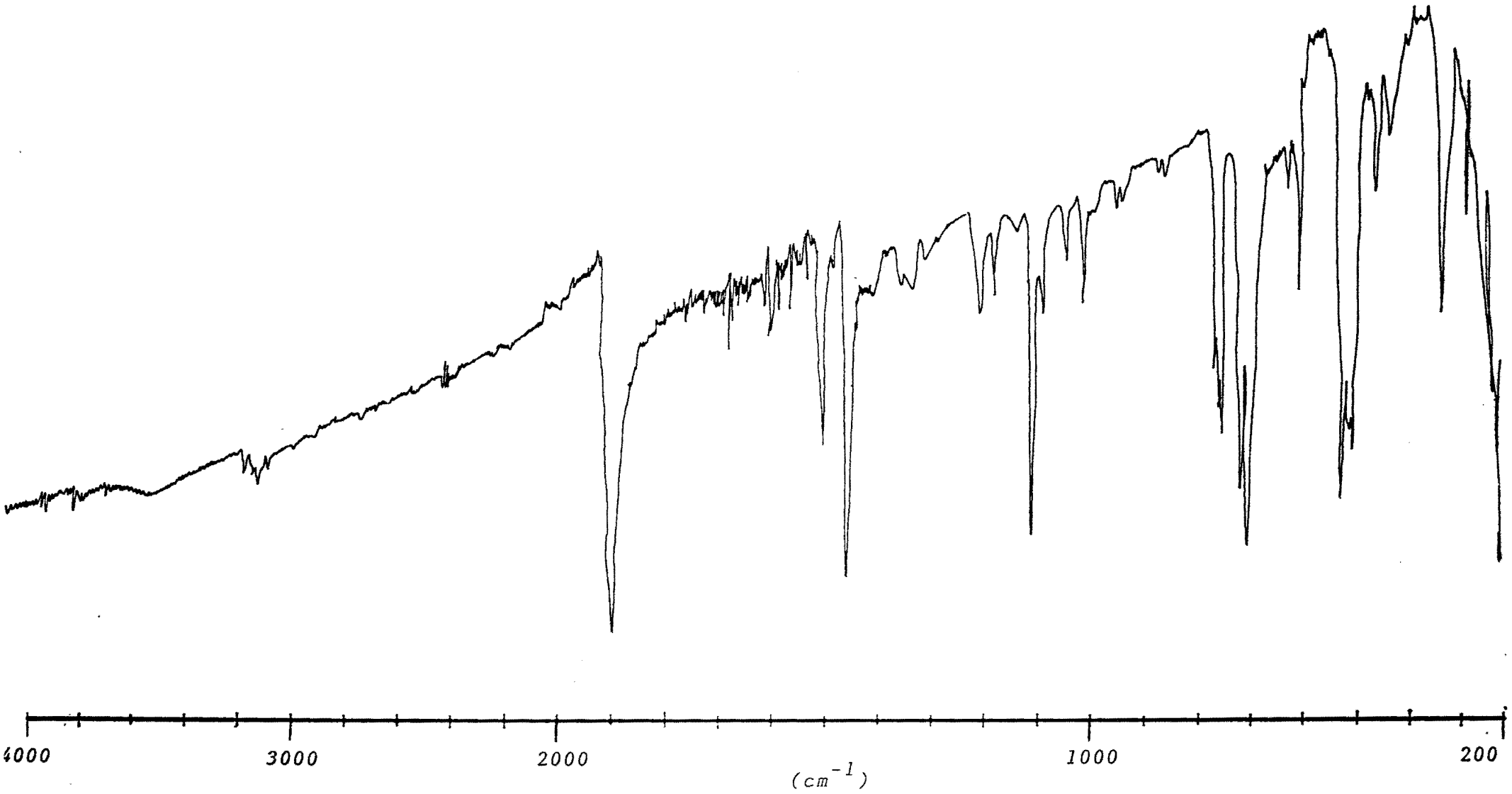


FIGURE 4.1

Infrared spectrum of $Ru(NO)Cl_3(PPh_3)_2$

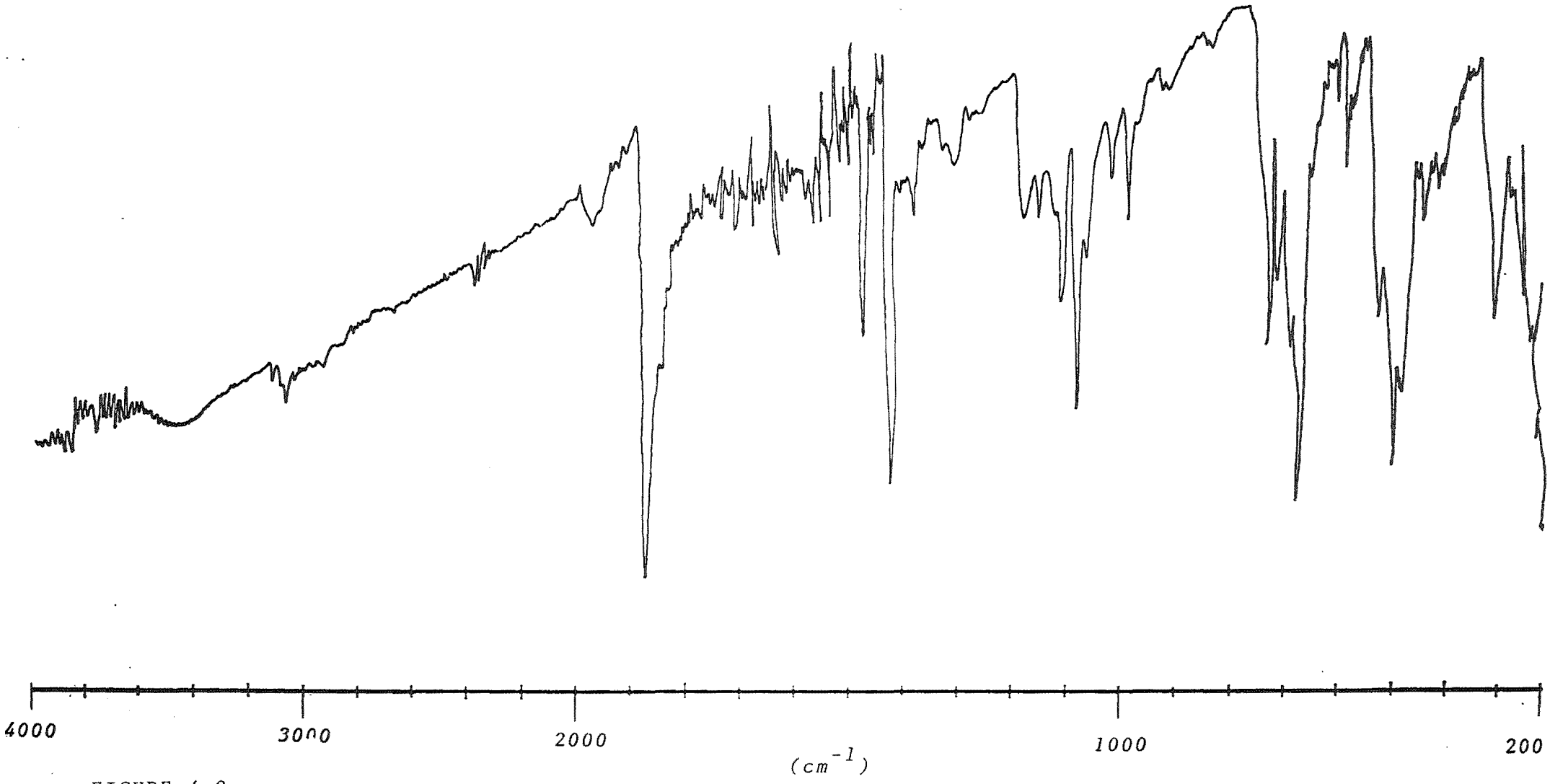


FIGURE 4.2

Infrared spectrum of $Ru(NO)Cl_3(PPh_3)_2$ *after irradiation*

reaction products for $Ru(NO)Br_3(PPh_3)_2$ as well as the results from the oxidation of the free ligand. The loss of some nitric oxide in the photochemical oxidation reaction of organosulphide complexes resulted in the formation of a tris-organosulphide complex when the organosulphide was present in excess. If an analogous tris-triphenylphosphine complex is formed, the fact that there is a decrease in rate of loss of NO when excess PPh_3 is present, suggests that this step proceeds by a dissociative mechanism.

4.3 THE PHOTOCHEMISTRY OF TRIHALOGENO(NITROSYL)-BIS(DIETHYLPHENYLPHOSPHINE)RUTHENIUM(II) COMPLEXES

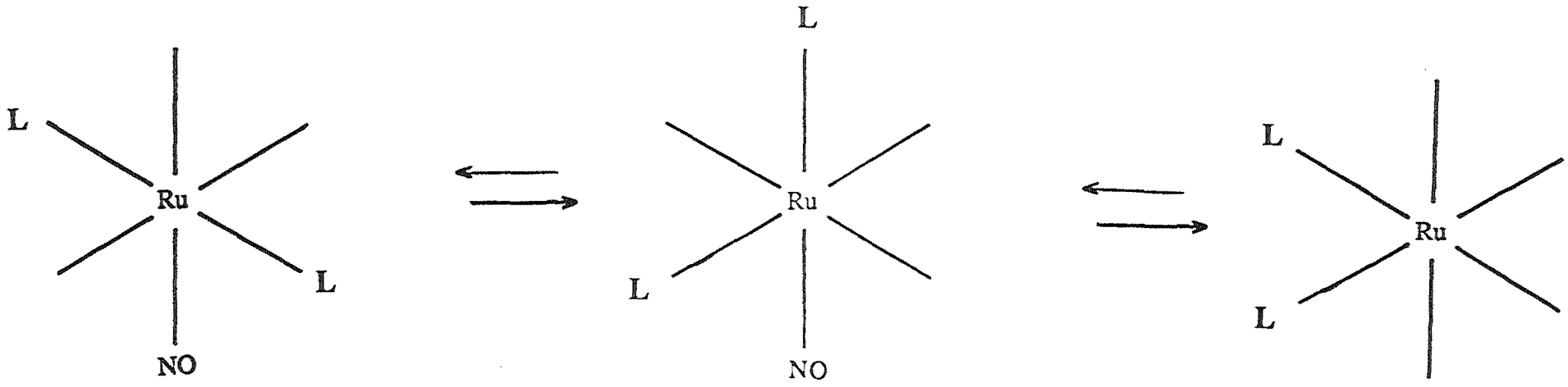
$Ru(NO)X_3(Et_2PPh)_2$ for X = Cl, Br, I

4.3.1. Introduction

Many photochemical reactions of transition metal complexes are isomerisations and ligand substitution reactions [Waltz & Sutherland 1972]. There has been only one report of a photochemical reaction involving a complex of the type investigated here. Innorta and Modelli (1978) studied the organophosphine complex $Ru(NO)Cl_3(Me_2PPh)_2$ and interpreted the spectral results in terms of a photochemical isomerisation illustrated in Scheme 4.1. Townsend & Coskran (1971) have reported that the complexes cis, fac - $Ru(NO)Cl_3(Me_2EPh)_2$, for E = P, and As were converted into the trans isomer by heating.

4.3.2 Virtual Coupling in Organophosphine Compounds

Since the ^1H n.m.r. spectra of organophosphine compounds is often complicated by virtual coupling [Randall & Shaw 1962; Musher & Corey



(A) trans isomer *(B) cis meridional isomer* *(C) cis facial isomer*

$$(A) + h\nu \rightleftharpoons (B)$$

SCHEME 4.1

Isomerisation reaction for $Ru(NO)Cl_3(Me_2PPh)_2$ **L** = Me_2PPh

1965; Narasimhan & Rogers 1961; Laing & Roper 1970], it is necessary to give a brief description of virtual coupling before discussing the results.

Virtual coupling occurs when the following conditions are obeyed;

$$\delta P_1 = \delta P_2 \text{ and } J(P_1 - P_2) \geq J(P_2 - H)$$

If the proton is coupled to P_2 but not to P_1 (because for example it is too far away) the effect of virtual coupling is to make it appear as if there is some coupling interaction between the proton and P_1. The effect is as if the proton was coupled to two equivalent nuclei.

Even though the above conditions are met when the complexes are in either the trans or cis facial configuration, most workers claim that the trans isomer is the preferred one (see Section 4.3.3)

4.3.3 ^{13}C and ^{1}H n.m.r. Study of Trihalogeno(nitrosyl)bis(diethylphenylphosphine)-ruthenium(II) Complexes

The diethylphenylphosphine complexes investigated in this work are readily soluble in chloroform and the ^{1}H n.m.r. spectra were measured for the chloro-, bromo-, and iodo- complexes. The ^{1}H n.m.r. spectrum of the bromo- complex is shown in Figure 4.3. In order to assign the resonances a series of decoupling experiments were carried out on the bromo- complex. The methylene protons showed a total of 13 peaks when no decoupling was applied. This multiplicity may arise from the overlap of multiplets shown in Figure 4.4. The triplets

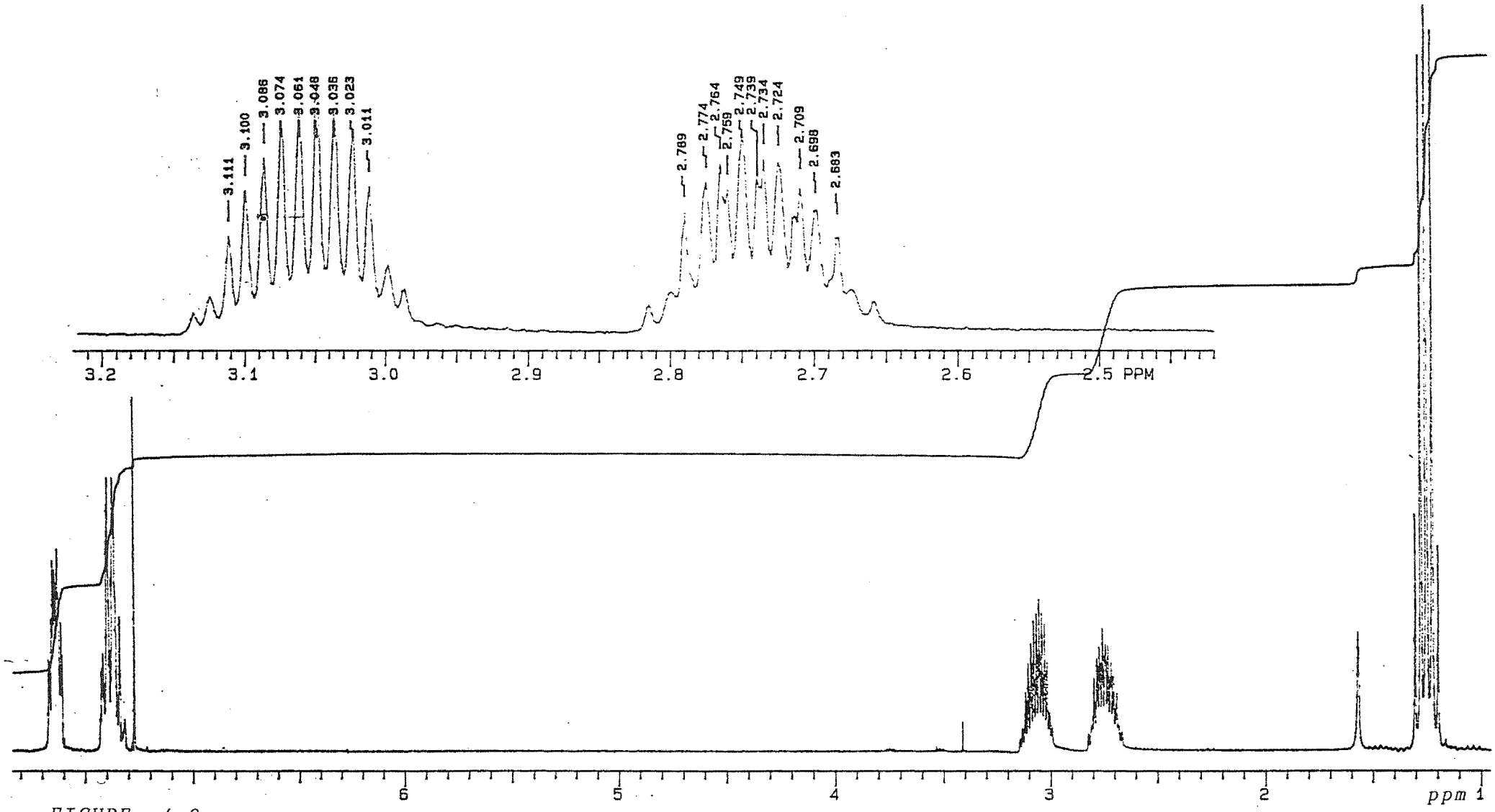


FIGURE 4.3

^{1}H *n.m.r. spectrum for* $Ru(NO)Br_3(Et_2PPh)_2$

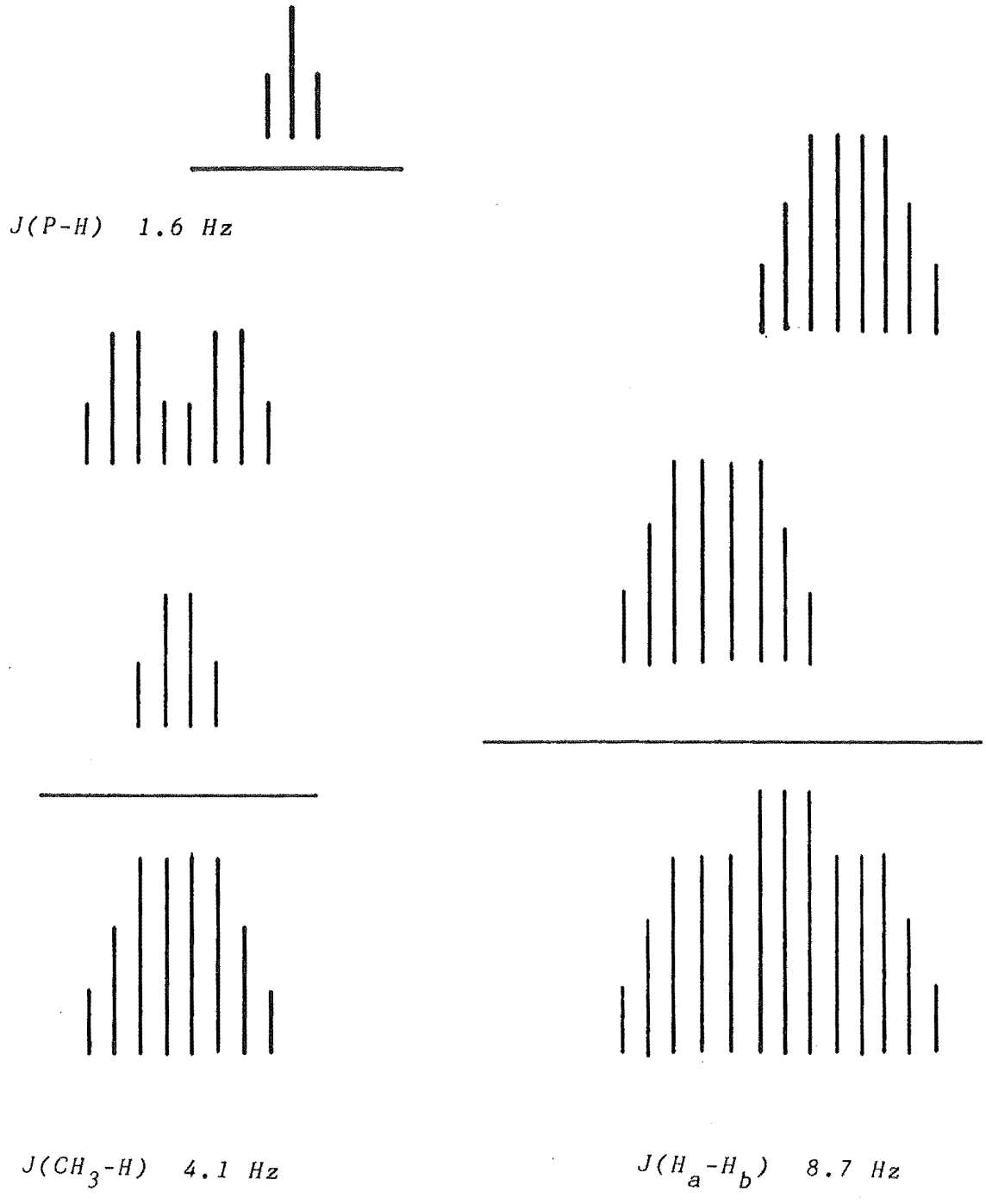


FIGURE 4.4

Multiplet pattern for methylene protons for $Ru(NO)Br_3(Et_2PPh)_2$

(which result from the phosphorus nuclei) are split by the methyl protons into three quartets that overlap to give a 1 2 3 3 3 3 2 1 octet. The coupling with the other methylene proton gives rise to two octets that overlap to give a total of 13 peaks 1 2 3 3 3 4 4 4 3 3 3 2 1. The two separate 13 peak multiplets are due to the two different environments of the inequivalent methylene protons. There is some evidence of slight splitting of these resonances, which may be due to the fact that the coupling constants are not exact multiples of each other. The methyl multiplet arises from the overlap of three triplets as shown in Figure 4.5 to give a 1 3 4 3 1 quintet.

When the methyl protons were decoupled, the 13 peaks collapsed into two doublets of triplets (Figure 4.6(A)). This would result from the splitting by the virtually coupled phosphorus nuclei giving rise to triplets, which are further split by the inequivalent methylene protons. Decoupling of either of the methylene protons led to a sextet for the methyl region as shown in Figure 4.6(B). This is a result of the methyl protons being split by the phosphorus nuclei and then again by the one other methylene proton. The other methylene region is also effected by this decoupling but it is not clear what the multiplicity of this resonance is.

This assignment is supported by the ^{13}C n.m.r. spectrum (Figure 4.7) which showed two resonances at δ = 7.30 and 12.70 ppm. Both of these were triplets and are assigned to the methyl and methylene carbons. The triplets are due to virtual coupling with the phosphorus nuclei.

The single crystal X-ray structure of the complex $Ru(NO)Br_3(Et_2PPh)_2$ complex was determined (see Chapter 7) and the phosphine ligands were found to be in the trans configuration, which

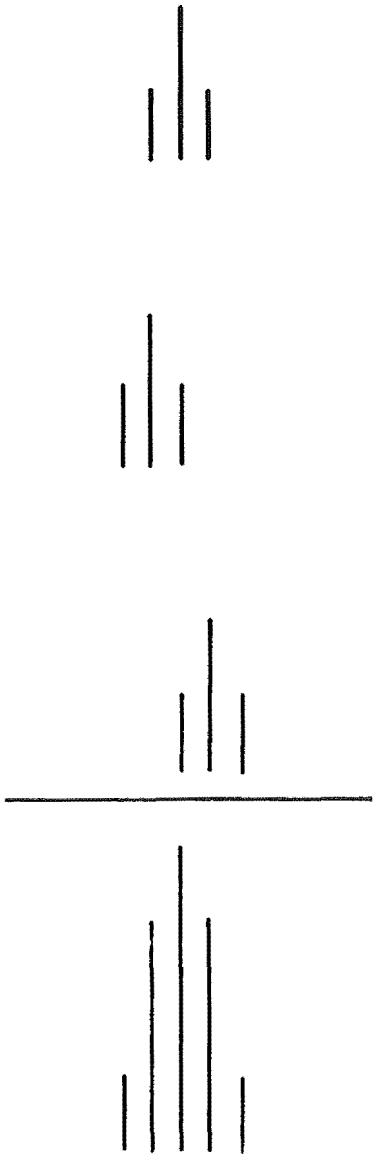


FIGURE 4.5

Multiplet pattern for methyl protons for $Ru(NO)Br_3(Et_2PPh)_2$

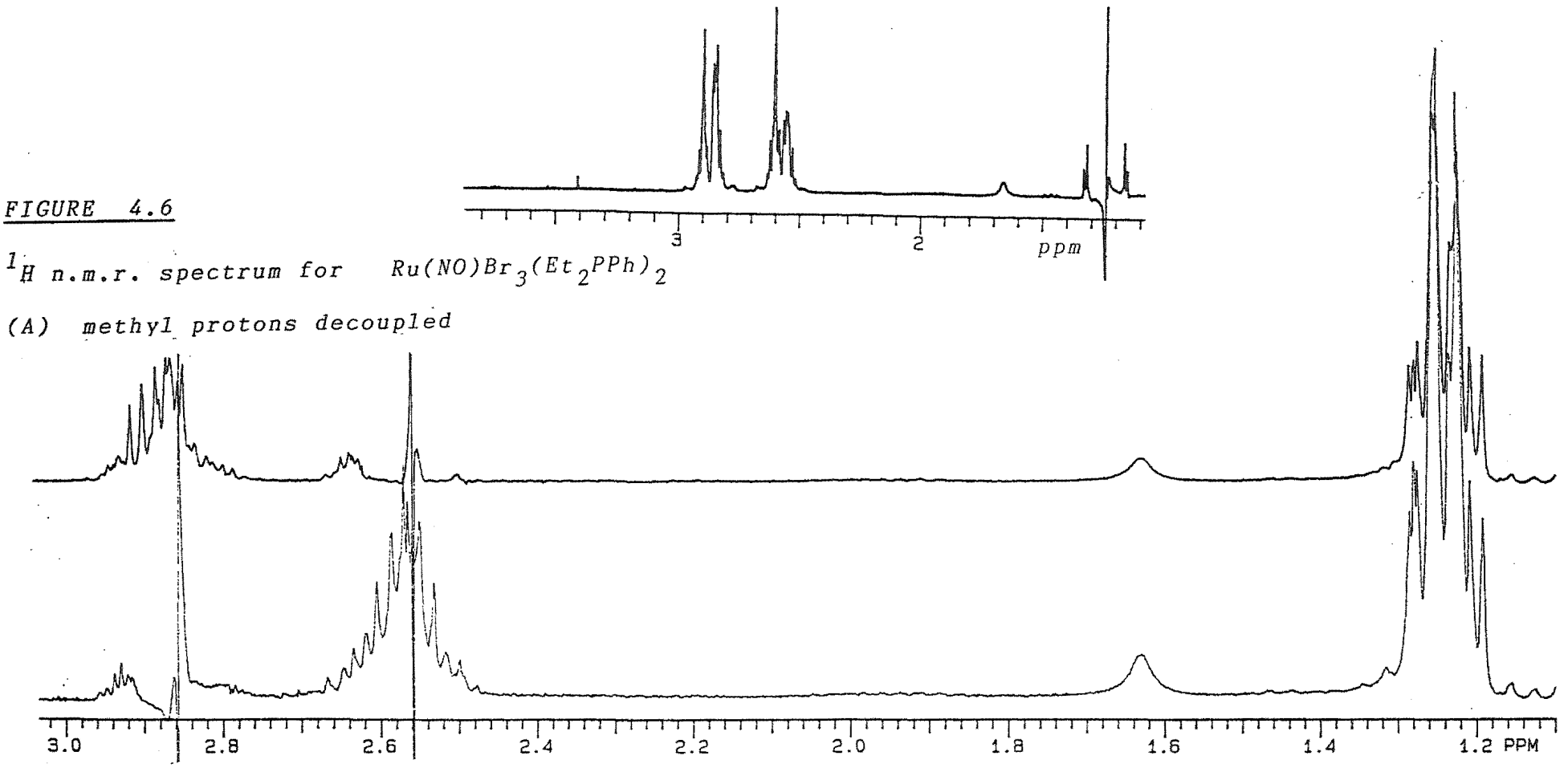


FIGURE 4.6

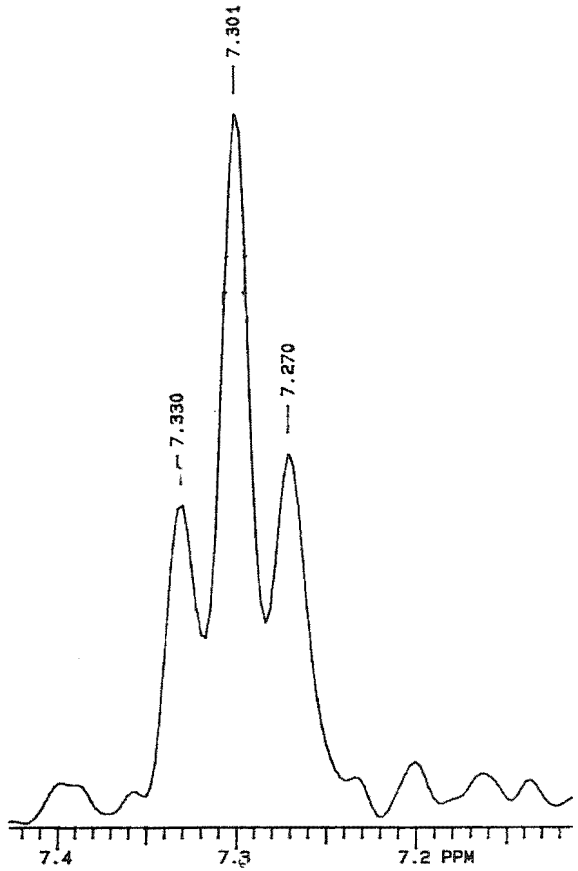
^{1}H *n.m.r. spectrum for* $Ru(NO)Br_3(Et_2PPh)_2$

(A) methyl protons decoupled

FIGURE 4.6

^{1}H *n.m.r. spectrum for* $Ru(NO)Br_3(Et_2PPh)_2$

(B) methylene protons decoupled



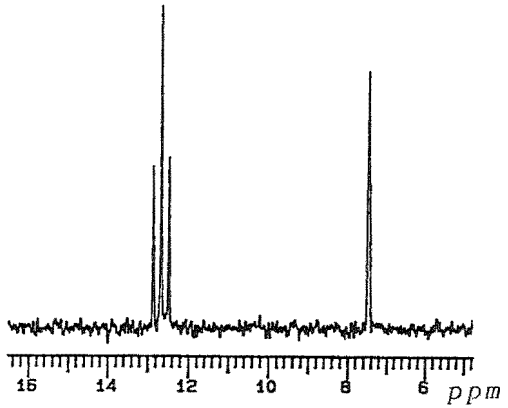


FIGURE 4.7

^{13}C n.m.r. spectrum for $Ru(NO)Br_3(Et_2PPh)_2$

is similar to the methyldiphenyl complex determined by Schultz et al. (1974) and in the triphenylphosphine complex as determined by Haymore & Ibers (1975a). The chloro- and iodo- complexes show identical ^1H n.m.r. and infrared spectra and have very similar X-ray powder diffraction patterns to that of the bromo- complex. Thus it seems likely that the three complexes all have the same configuration.

Chatt and Wilkins (1952) suggested that the cis isomer would be favoured because in this configuration the two phosphorus atoms are opposite weak π-acceptors. Schultz et al. (1974) claim however that steric constraints control the arrangement of the organophosphine ligands and that for bulky ligands the trans isomer is preferred. Complexes with the cis arrangement have been reported [Townsend & Coskran 1971] for the complexes $Ru(NO)Cl_3(Me_2PPh)_2$ and $Ru(NO)Cl_3(Me_2AsPh)_2$ but they are readily converted into the trans isomer when heated.

4.3.4 Free Ligand Studies

The oxidation of diethylphenylphosphine may be accomplished with dioxygen, either by heating or using UV radiation [Geoffroy et al. 1976b]. It was observed in the present work that NO or O_2 would also oxidise diethylphenylphosphine to diethylphenylphosphineoxide. The product was identified by the appearance of two new resonances in the ^1H n.m.r. spectrum; a triplet at δ = 1.22, a quartet at 3.69 ppm, and a shift in the phenyl resonance to 7.70 ppm. The infrared spectrum showed two new strong resonances at 1120 and 1190 cm^{-1}. The reaction of diethylphenylphosphine with nitrogen dioxide, in addition to changes similar to those found above, also showed substantial changes

to the phenyl region of the ^{1}H n.m.r. spectrum. This result suggests that the reaction may involve more than the production of diethylphenylphosphineoxide. One possibility is that nitration of the aromatic group has occurred. The resonance was shifted down field relative to the starting material to 7.57 ppm consistent with the formation of a nitrated phenyl compound [Pouchert & Campbell 1974]. The infrared spectrum showed new strong absorbances at 1300 cm^{-1} and 1650 cm^{-1} which is the correct region for the presence of NO_2 [Bellamy 1975].

4.3.5 The Photochemical Reaction of Trans-[tribromo(nitrosyl)bis(diethylphenylphosphine)-ruthenium(II)]

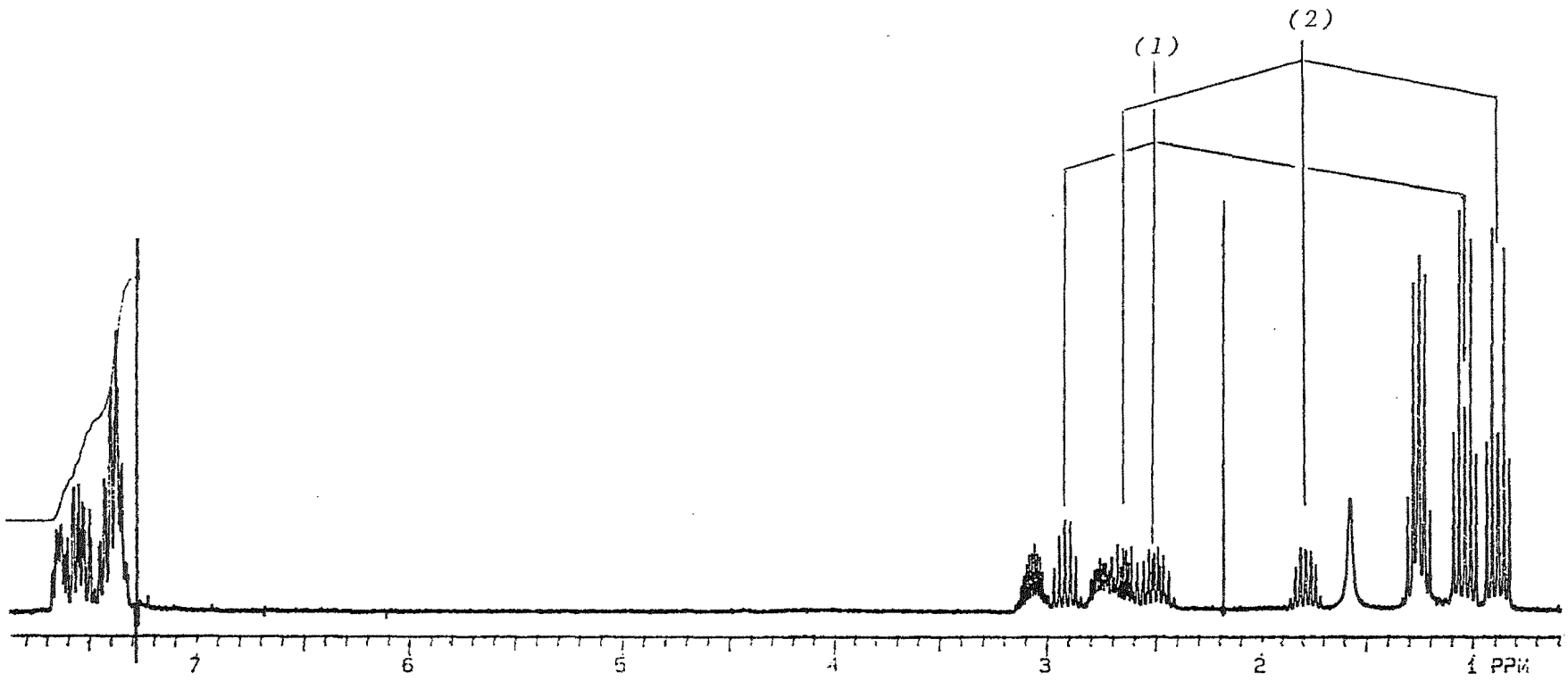
The complex $Ru(NO)Br_3(Et_2PPh)_2$ was dissolved in reagent grade chloroform and when exposed to sunlight, a rapid reaction occurred with the solution changing from orange to a deep green colour within a few hours. The solvent was removed under vacuum and the solid products analysed using infrared and n.m.r. spectroscopy.

The infrared spectrum of the products showed no significant changes compared with the starting material. The gaseous products were analysed by mass spectrometry and did not provide evidence for the existence of nitric oxide, nitrogen dioxide, or dinitrogenoxide. Therefore it appeared that oxidation had not occurred. The elemental analytical results for the solid products suggested that no significant stoichiometric changes had occurred. Found: C = 34.6%, H = 5.1%; Calculated for $Ru(NO)Br_3(Et_2PPh)_2$ [$C_{20}H_{30}Br_3NOP_2Ru$]; C = 34.2, H = 4.3%.

On the other hand the ^1H n.m.r. spectrum of the reaction products (Figure 4.8) indicated that substantial changes had occurred. There appeared four new septets at; δ = 1.80 ppm, 2.50ppm, 2.65ppm and 2.92 ppm, and two new quintets at δ = 0.9 ppm and 1.05 ppm.

These changes can be interpreted as an isomerisation reaction leading to the formation of a cis meridional isomer similar to that observed by Innorta and Modelli (1978). A series of decoupling experiments made it possible to identify the septets and to decide which septet was associated with the quintets (Figure 4.9). The quintet at 0.90 ppm is coupled to the septets at 1.80 ppm and 2.65 ppm, and the quintet at 1.05 ppm is coupled to the septets at 2.50 ppm and 2.92 ppm. One set of coupled resonances would be due to the Et_2PPh group opposite the NO and the other resonances to the Et_2PPh opposite the bromine. The relationship between these resonances and their assignment is indicated in Figure 4.8. The methylene peaks now appear as septets rather than 13 peaks as was observed when virtual coupling occurred. This may arise from the overlap shown in Figure 4.10. Two quartets, arising from the splitting by the other methylene proton, overlap to give a 1 3 4 3 1 quintet. The two quintets, arising from the splitting by the single coupled phosphorus nuclei, overlap to give a 1 3 4 5 4 3 1 septet. The two separate septets are due to the two different environments of the inequivalent methylene protons.

The methyl protons appear as 1 3 2 3 1 quintets. The quintets may arise from the formation of a triplet, from the methylene protons, which is split by coupling with the phosphorus nuclei to give two triplets.



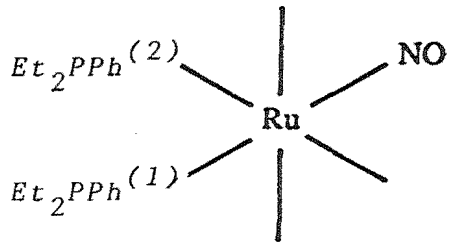


FIGURE 4.8

^{1}H *n.m.r spectrum for* $Ru(NO)Br_3(Et_2PPh)_2$ *after irradiation*

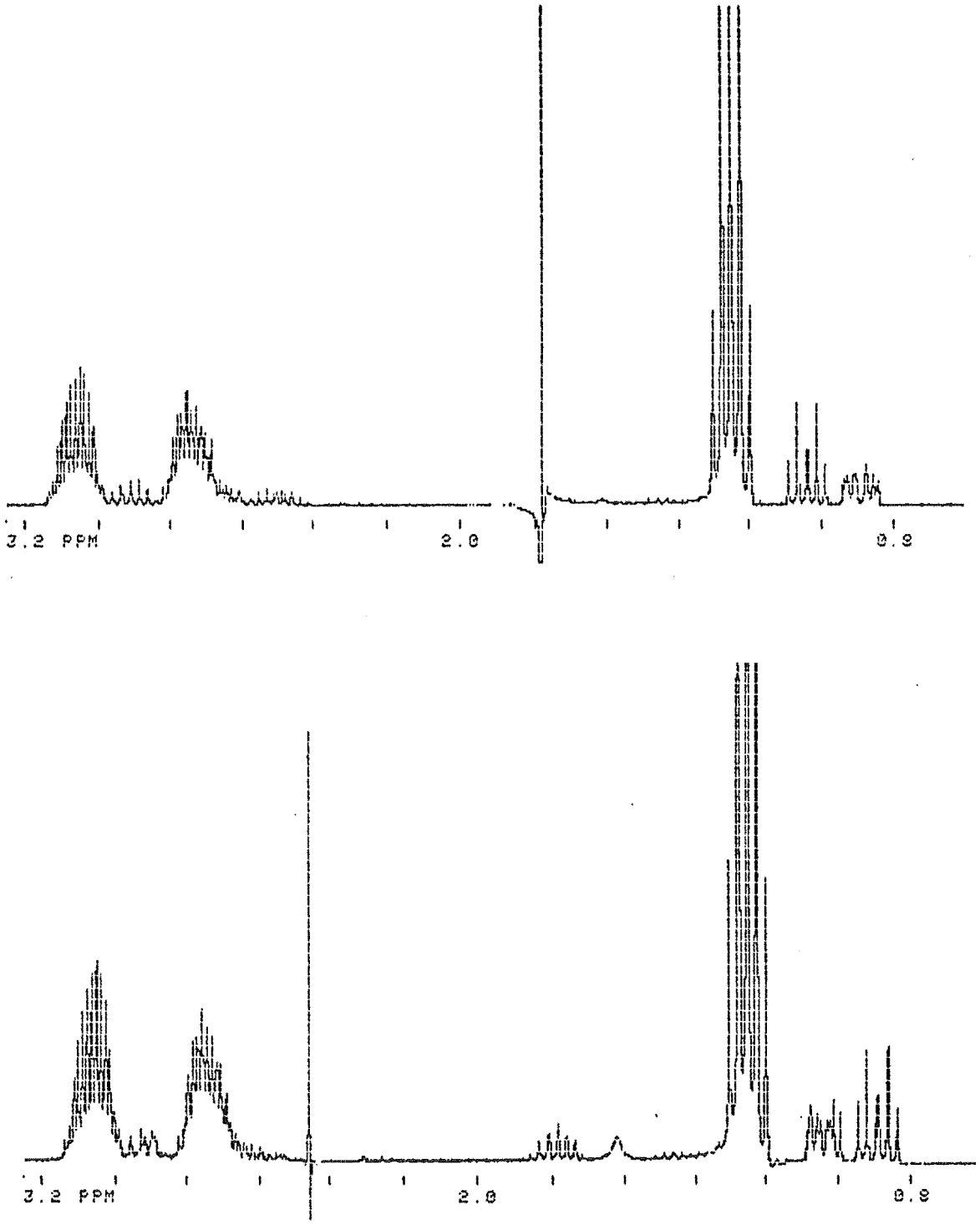


FIGURE 4.9

^{1}H n.m.r. spectrum for $Ru(NO)Br_3(Et_2PPh)_2$ after irradiation, with methylene protons decoupled

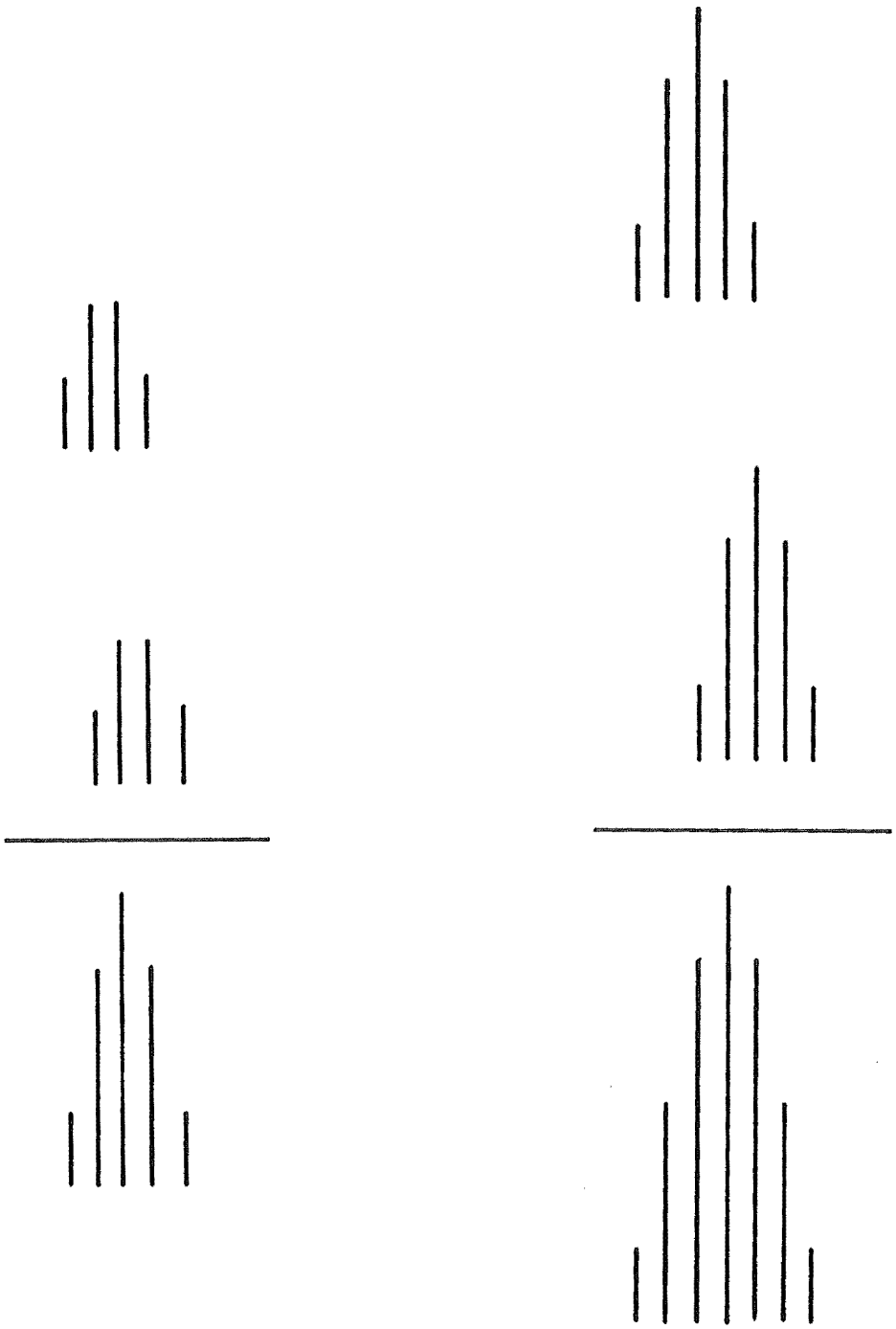


FIGURE 4.10

Multiplet pattern for methylene protons for $Ru(NO)Br_3(Et_2PPh)_2$ *after irradiation*

4.3.6 The Photochemical Reaction of Trans-[trichloro(nitrosyl)bis(diethylphenylphosphine)-ruthenium(II)] and Trans-[triiodo(nitrosyl)bis(diethylphenylphosphine)-ruthenium(II)]

The complexes $Ru(NO)X_3(Et_2PPh)_2$ for X = Cl, I underwent a similar colour change upon exposure to sunlight. The ^1H n.m.r. spectra were measured on the reaction products after the removal of the solvent and they showed similar changes to that discussed above for the bromo-complex. No changes were observed in the infrared spectra of the solid reaction products. The elemental analytical results for the chloro- complex suggested that there had been little change in the stoichiometry. Found: C = 40.8%, H = 6.6%; Calculated for $Ru(NO)Cl_3(Et_2PPh)_2$ [$C_{20}H_{30}Cl_3NOP_2Ru$]; C = 42.1%, H = 5.3%. This suggests that the same type of photochemical isomerisation reaction has occurred for all three complexes, namely the formation of the cis meridional isomer.

In addition to the two distict methylene resonances, in the ^1H n.m.r. spectrum of the iodo- starting material, a small extra multiplet centred at δ = 3.15 ppm was observed. This multiplet was still present after recrystallisation of the complex, and the infrared spectrum and elemental analytical results showed no evidence of any impurity (see Table 4.1 in the experimental). It is possible that this resonance is due to the presence of a small amount of the cis facial isomer. When the iodo- complex was irradiated all three resonances were reduced in intensity as the new resonances due to the formation of the cis meridional isomer appeared.

In one experiment under the same reaction conditions, irradiation of the iodo- complex resulted in a product whose ^{1}H n.m.r. spectrum indicated a loss in intensity of all three of the original multiplets, and the appearence of new multiplets in the positions expected for uncoordinated diethylphenylphosphineoxide. The infrared spectrum of this product had absorbances at 1120 cm^{-1} and 1180 cm^{-1}, consistent with the presence of diethylphenylphosphineoxide. Because alkylphosphines are readily oxidised by either dioxygen or nitrogen oxides, it is surprising that oxidised compounds were not obtained more readily and that there was no evidence for oxidation in the bromo- and chloro- complexes. The oxidation of the diethylphenylphosphine may involve dissociation of the ligand from the complex which is more likely to occur for the iodo- complex due to the greater steric bulk of the iodo- ligands.

Attempts to separate the isomers of $Ru(NO)Br_3(Et_2PPh)_2$ using radial chromatography were unsuccessful. Even though the trans isomer (the starting material) was easily eluted using chloroform (identified by its ^{1}H n.m.r. spectrum), the other products could not be shifted from the plate.

PART B

THE PREPARATION AND PHOTOCHEMISTRY OF ORGANOSULPHIDE AND ORGANOPHOSPHINE COMPLEXES OF OSMIUM

4.4 THE PREPARATION AND PHOTOCHEMISTRY OF TRIHALOGENO-(NITROSYL)BIS(ORGANOPHOSPHINE)OSMIUM(II) COMPLEXES $Os(NO)X_3(PR_3)_2$ for X = Cl, Br.

4.4.1 The Photochemistry of Trihalogeno(nitrosyl)bis(triphenylphosphine)-osmium(II) Complexes

The chloro- and bromo- complexes $Os(NO)X_3(PPh_3)_2$ were prepared and both displayed a colour change when chloroform suspensions of the complexes were exposed to sunlight. Neither of the complexes are soluble in chloroform and the ^1H n.m.r. spectra of the starting materials were unable to be measured. Upon irradiation the pale orange suspension of the chloro- complex became a dark orange solution. For the bromo- complex the mixture went from an orange precipitate to a pink coloured solution. After irradiation the solvent was removed under vacuum and the solid products analysed using infrared and n.m.r. spectroscopy. The infrared spectra showed evidence for oxidation of the triphenylphosphine, with the appearance of two new absorbances (1120 and 1180 cm^{-1}) for both complexes. The presence of the absorbance at 1180 cm^{-1} in the infrared spectra suggests that free triphenylphosphineoxide has formed (see Section 4.2.2). For both complexes there are two new absorbances (at 720 and 560 cm^{-1}) similar to that discussed for the ruthenium complexes

$Ru(NO)X_3(PPh_3)_2$ described in Section 4.2 and this indicates that some of the triphenylphosphineoxide that has been formed is coordinated to the osmium. The absorption at 1180 cm^{-1} only occurs after long irradiation times which suggests that the triphenylphosphineoxide was first coordinated and then lost from the complex.

There is evidence for at least three phenyl resonances in the ^1H n.m.r. spectrum which could be due to the starting material, some coordinated oxide, and the uncoordinated oxide.

The analytical results of the solid products after a short irradiation time (6 days) are reasonably close to the calculated values for complexes of the type $Os(NO)X_3(PPh_3)(OPPh_3)$. Found: C = 47.9%, H = 4.3%; Calculated for $Os(NO)Cl_3(PPh_3)(OPPh_3)$ $[C_{36}H_{30}Cl_3NO_2P_2Os]$; C = 49.9%, H = 3.5%. Found: C = 44.0%, H = 4.5%; Calculated for $Os(NO)Br_3(PPh_3)(OPPh_3)$ $[C_{36}H_{30}Br_3NO_2P_2Os]$; C = 43.2%, H = 3.0%.

4.4.2 The Preparation of Trihalogeno(nitrosyl)bis(diethylphenylphosphine)osmium(II) Complexes

Preparation of the osmium analogues of the ruthenium complexes $Ru(NO)X_3(Et_2PPh)_2$ proved difficult. The method that produced a crystalline material was that of Araneo et al. (1970) which involved the treatment of $A_2[OsX_6]$ in 2-methoxyethanol with NO followed by reaction with Et_2PPh. This method, when used for PPh_3 produced good yields of pure $Os(NO)X_3(PPh_3)_2$ for X = Cl, Br. However, for diethylphenylphosphine, mixtures were obtained with poor analytical results for the required products. Found: C = 34.4%, H = 4.7;

Calculated for $Os(NO)Cl_3(Et_2PPh)_2$ [$C_{20}H_{30}Cl_3NOP_2Os$]; C = 36.4%, H = 4.6%. For the preparation of $Os(NO)Cl_3(Et_2PPh)_2$ the infrared spectrum of the product obtained showed two absorbances attributable to ν(NO) at 1840 and 1800 cm^{-1}, and a strong absorbance at 1090 cm^{-1}. The ^1H n.m.r. spectrum suggested that a mixture of compounds had been formed, which may have arisen from oxidation during the preparation. Recrystallisation resulted in two crystalline materials; a small quantity of flakey orange crystals, and a larger quantity of larger block shaped orange crystals. The block shaped crystals were analysed by single crystal X-ray diffraction and the complex found to be $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$ which contains a coordinated 2-methoxyethanoate ligand (see Chapter 7). Oxygen ethers have an absorbance in infrared spectrum in the range 1060 - 1150 cm^{-1} and the infrared spectrum for 2-methoxyethanol was measured and showed absorbances at 1065 and 1120 cm^{-1}. This work highlights the need for caution in interpreting infrared results, as similar absorbances may also occur for a complex containing a coordinated diethylphenylphosphineoxide ligand.

The chloro- and bromo- complexes $Os(NO)X_3(Et_2PPh)_2$ were unable to be isolated as pure compounds. The method of Robinson & Uttley (1972) was also attempted but failed to produce any crystalline material.

The small flakey crystals obtained during the preparation of $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$ were separated under a microscope and their infrared spectrum was found to be very similar to that of $Ru(NO)Cl_3(Et_2PPh)_2$. Only a very small quantity of this material was obtained and no furthur studies were carried out on it.

4.5 THE PREPARATION OF TRIHALOGENO(NITROSYL)-BIS(ORGANOSULPHIDE)OSMIUM(II) COMPLEXES

In this section attempts to prepare complexes of the form $Os(NO)X_3(R_2S)_2$ for X = Cl, Br are described.

The salts $A_2[OsX_6]$ were dissolved in 2-methoxyethanol and NO gas passed through the solution for several hours and then left overnight. The solvent was removed under vacuum and the residue taken up in ethanol, diethylsulphide was added and the mixture heated under reflux. The dark brown solution changed in colour to a bright red colour and the solvent volume was reduced under vacuum. No crystalline product was obtained and the infrared spectrum was measured on the resulting oil. The spectrum had a strong absorbance at 920 cm^{-1} for the bromo- and 910 cm^{-1} for the chloro- which is typical for ν(SO) [Bellamy 1968; Bellamy 1975].

The preparation was repeated but this time the solvent was allowed to evaporate at room temperature and atmospheric pressure. Small bright red thin plate crystals were obtained after about a month. The single crystal X-ray structure was determined on the bromo- complex and it was found to be a mixed diethylsulphide diethylsulphoxide nitrosyl complex $Os(NO)Br_3(Et_2S)(Et_2SO)$, which is isostructural with the ruthenium complex discovered by Page (1978) (see Chapter 7).

It is likely that NO_2 is the oxidising agent as was discovered for the ruthenium case, because after the addition of the Et_2S the reaction mixture was heated and a brown gas appeared in the condenser. This suggests that there is some loss of nitric oxide from the complex in contrast to the ruthenium preparation, and may explain why

oxidation of the diethylsulphide ligands occurs more readily for the osmium complexes than the ruthenium complexes. Several attempts to repeat the preparations of the osmium bromo- and chloro- nitrosyl diethylsulphide diethylsulphoxide complexes on a larger scale were unsuccessful, and no crystalline products were obtained.

A similar preparation using diphenylsulphide failed to produce any crystalline material. The preparation of the diethylsulphide complex was also attempted in the presence of a reducing agent. The '$Os(NO)X_n$' entity was made and then heated under reflux with diethylsulphide in the presence of sodium sulphite. The resulting black precipitate showed no evidence of NO in the infrared spectrum.

The preparation was also attempted using MNTS as the nitrosylating agent. A bright orange powder was isolated which had an infrared spectrum very similar to that of the ruthenium complex $RuCl_3(Et_2S)_3$ and whose ^1H n.m.r. spectrum was composed of broad peaks suggesting the presence of a paramagnetic species. There was no evidence for an absorbance assignable to V(NO) in the infrared spectrum. The infrared and n.m.r. spectra are consistent with the formation of $OsCl_3(Et_2S)_3$.

4.6 EXPERIMENTAL

4.6.1 Preparation of the Ligands and Reagents

a) Organophosphines

Triphenylphosphine, triphenylphosphineoxide and diethylphenylphosphine were obtained commercially [Aldrich] and used without furthur purification. Organophosphines may be prepared from Grignard reactions [Jensen et al. 1963; Davies et al. 1929; Adams & Raynor 1965].

b) Diethylsulphide

Diethylsulphide was obtained commercially [Koch Light] and used without further purification.

c) Nitric oxide

Nitric oxide was prepared as outlined in Chapter 3.

d) Iron(II)chloride 4-hydrate

The compound $FeCl_2 \cdot 4H_2O$ was prepared from the reaction of pure electrolytic grade iron metal (25g) with an excess of 12M HCL (200ml). The solution evolved hydrogen gas rapidly, and large pale green crystals of iron(II)chloride 4-hydrate separated out. These crystals were washed with chloroform and were dried under vacuum. The compound was used immediately before any oxidation occurred.

4.6.2 Preparation of the Complexes

a) Trihalogeno(nitrosyl)bis(organophosphine)ruthenium(II)

$Ru(NO)X_3(PPh_3)_2$ for X = Cl, Br, I.

There have been many reports of the preparation of the organophosphine complexes studied here [Townsend & Croskran 1971; Fairey & Irving 1966; Chatt & Shaw 1966; Haymore & Ibers 1975a; Robinson & Uttley 1972; Taqui Khan & Mohiuddin 1983; Pandey et al. 1982; Schultz et al. 1974; Baird 1971; Heveldt 1975; Ashok et al. 1985a; Ashok et al. 1985b; Ahmad et al. 1974a]. A modification of the method of Haymore and Ibers (1975a) was used, based on the intial preparation of the '$Ru(NO)Cl_3$' entity. This was found to be most successful when the ethanol solution of $RuCl_3 \cdot 3H_2O$ was flushed with nitric oxide gas for long periods of time (at least four hours) and then left to stand overnight in the saturated solution. The solvent was then removed under vacuum and the viscous residue taken up in 2-methoxyethanol. The complex was then prepared by adding the organophosphine in a three times molar excess to a boiling solution of '$Ru(NO)Cl_3$' or '$Ru(NO)Br_3$' in 2-methoxyethanol. The complex precipitated immediately and the solution was heated under reflux for a further 15 minutes to ensure completion of the reaction. The yield was typically 80% to 90%, and the elemental analytical results were in good agreement with the calculated values.

b) Ammonium hexabromoosmate(IV)

$(NH_4)_2[OsBr_6]$

The complex $(NH_4)_2[OsBr_6]$ was prepared by the method of Dwyer & Hogarth (1957a). A 1g ampoule of osmium(VIII) oxide was broken into a 100ml Erlenmeyer flask containing 36ml of 47% HBr. The solution was heated under reflux for 2 hours and decanted from the broken ampoule. The flask was rinsed with an extra 7ml of HBr and 3g of ammonium bromide added to the hot solution. The solution was allowed to cool to room temperature and 50ml of ethanol added. A black precipitate formed which settled in the flask. The solid was thoroughly washed with ethanol until free from halide as tested with ethanolic silver nitrate. The yield was almost quantitative and the complex was identified by it's UV-visible spectrum [Jorgenson 1962].

c) Ammonium hexachloroosmate(IV)

$(NH_4)_2[OsCl_6]$

The complex $(NH_4)_2[OsCl_6]$ was prepared in a similar manner to the bromo- analogue [Dwyer & Hogarth 1957b]. Osmium(VIII)oxide 1g was added to a solution of iron(II)chloride 4-hydrate (10g) in 12M HCl (30ml) and heated on a water bath for two hours. The soution was decanted and the flask rinsed with excess 12M HCl (10ml). Ammonium chloride solution 20% (10ml) was added and the mixture cooled with ice. This resulted in a bright red precipitate which was washed thoroughly with ethanol untill free from halide. The yield was almost quantitative and the complex was identified by it's UV-visible spectrum [Jorgenson 1962].

d) Sodium hexachloroosmate(IV)

$Na_2[OsCl_6]$

The preparation of the complex $Na_2[OsCl_6]$ was attempted by a method analogous to that used for the ammonium salt without success. The preparation was however achieved by using a cation exchange column. Ammonium hexachloroosmate(IV) (0.25g) as prepared above was dissolved in double distilled water and passed through a protonated cation exchange column (Dowex 50-X8). The cation exchange column was prepared by making a slurry of the resin in double distilled water (40ml) and packing this into a burette evenly to reduce the formation of voids. The resin was protonated by passing 0.1M HCl (100ml) through very slowly and then rinsing with a large volume (at least one litre) of double distilled water. The ammonium complex was then passed down the column and the effluent collected. The column effluent was passed through the column again to ensure that all the ammonium cations were displaced and then the stoichiometric quantity of sodium chloride (0.067g) was added. The water was removed under vacuum yielding a blue solid. The residue was taken up in 2-methoxyethanol and used directly in the preparation of the organosulphide or organophosphine complexes.

e) Trichloro(nitrosyl)bis(triphenylphosphine)osmium(II)

$Os(NO)Cl_3(PPh_3)_2$

There are several reports of the preparation of complexes of the stoichiometric type $Os(NO)X_3(PPh_3)_2$ [Ahmad et al. 1974b; Araneo et al. 1970; Laing & Roper 1968b; Pandey et al. 1981b]. The method of Araneo et al. (1970) was used. Sodium hexachloroosmate(IV) (0.25g) prepared

above was dissolved in 2-methoxyethanol and flushed with nitric oxide gas for a total of 90 minutes while heating under reflux. The solution changed in colour from a dark brown to a bright red colour. Triphenylphosphine (1.5g) was added and a bright orange precipitate formed immediately. The precipitate was collected and washed with ethanol. The complex was recrystallised from a benzene/ethanol solvent mixture.

f) Tribromo(nitrosyl)bis(triphenylphosphine)osmium(II)

$Os(NO)Br_3(PPh_3)_2$

The complex $Os(NO)Br_3(PPh_3)_2$ was prepared in a similar manner to the chloro- complex using ammonium hexabromoosmate(IV) as the starting material and without heating. Ammonium hexabromoosmate(IV) is sparingly soluble in 2-methoxyethanol, and 200ml of the solvent was required to dissolve 0.4g of $(NH_4)_2[OsBr_6]$. The dark orange crystals were recrystallised as for the chloro- analogue. It is also possible to use the free acid that is formed in the effluent from the cation exchange column described above.

g) Trichloro(nitrosyl)bis(diethylphenylphosphine)osmium(II)

$Os(NO)Cl_3(Et_2PPh)_2$

The preparation of the complexes $Os(NO)X_3(Et_2PPh)_2$ was attempted in a similar manner to the triphenylphosphine complexes using the method of Araneo et al. (1970) and the method of Robinson and Uttley (1971). The method of Araneo et al. (1970) produced a mixture of large block shaped orange crystals and small flakey orange crystals. The block shaped crystals were found by single crystal X-ray

diffraction to be $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$. No crystalline material was isolated for either the bromo- or the chloro- preparation using the method of Robinson & Uttley (1971).

h) Trihalogeno(nitrosyl)(diethylsulphide)(diethylsulphoxide)-osmium(II) $Os(NO)X_3(Et_2S)(Et_2SO)$ for X = Cl, Br.

The complexes $Os(NO)X_3(Et_2S)(Et_2SO)$ were prepared in a similar manner to the organophosphine complexes. After addition of the nitric oxide to $A_2[OsX_6]$ the solution was flushed with dinitrogen for an hour and the solvent removed under vacuum and the residue taken up in fresh solvent. This was to ensure that there was no residual nitric oxide or nitrogen dioxide present since the intention was to produce a pure diethylsulphide complex. When the diethylsulphide was added the solution immediately changed colour to a bright red colour. The solution was heated under reflux for 30 minutes and the solvent removed under vacuum resulting in a viscous oil. Crystallisation was slow and after one to two months a small quantity of bright red thin rhombic shaped crystals appeared. The bromo- complex was analysed using single crystal X-ray diffraction and found to be isostructural with the ruthenium analogue.

i) Dichloro(nitrosyl)bis(diethylphenylphosphine)-(2-methoxyethanoate)osmium(II)
$Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$

Sodium hexachloroosmate(IV) (0.25g) was dissolved in 2-methoxyethanol (50ml) and flushed with NO gas for 90 minutes while heating under reflux. The mixture was flushed with dinitrogen for 30

minutes and diethylphenylphosphine (1.0ml) added. The solution was heated for a further 20 minutes and the solvent removed under vacuum. An orange crystalline material was obtained that was washed with ethanol. The material showed two clear absorbances for the nitrosyl grouping as well as a strong absorbance at 1090 cm^{-1} which can be assigned to the ether linkage. When recrystallised from chloroform two distinct crystalline forms were obtained, large block shaped crystals, and fine flakely orange crystals. The large block shaped orange crystals were analysed by single crystal X-ray diffraction and found to be the required product $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$. The peak at 1800 cm^{-1} is assigned to the nitrosyl group in this complex. There is evidence in the ^1H n.m.r. spectrum for an extra two CH_2 groups with a triplet at δ = 2.45 ppm and at 3.32 ppm. There is no obvious singlet that can be assigned to the methoxy group.

The smaller crystals were separated out under a microscope and found to have an infrared spectrum very similar to that of $Ru(NO)Cl_3(Et_2PPh)_2$.

4.6.3 Experimental Conditions for the Reactions of the Ligands and the Photochemical Reactions

The procedure and the reaction vessels used were the same as outlined in Chapter 3 for the studies of the free organosulphide ligands, and the organosulphide complexes.

Compound	^{1}H n.m.r. (ppm)	Infrared cm^{-1}	Elemental anal. C, H. Found (calculated)
$Ru(NO)Cl_3(PPh_3)_2$		1880 ν(NO)	56.2(56.7), 4.7(4.0)
$Ru(NO)Br_3(PPh_3)_2$		1885 ν(NO)	48.1(48.3), 3.4(3.4)
$Ru(NO)Cl_3(Et_2PPh)_2$	1.25(Q) 2.60(M),2.85(M)	1870 ν(NO)	42.1(42.2), 5.5(5.3)
$Ru(NO)Br_3(Et_2PPh)_2$	1.25(Q) 2.75(M),3.05(M)	1860 ν(NO)	34.5(34.2), 4.4(4.3)
$Ru(NO)I_3(Et_2PPh)_2$	1.25(Q) 3.03(M),3.34(M)	1855 ν(NO)	27.8(28.4), 3.7(3.6)
$Os(NO)Cl_3(PPh_3)_2$		1850 ν(NO)	50.6(50.8), 4.1(3.6)
$Os(NO)Br_3(PPh_3)_2$		1870 ν(NO)	43.5(43.9), 3.6(3.1)
$Os(NO)Cl_3(Et_2S)(Et_2SO)$		1840 ν(NO) 910 ν(SO)	
$Os(NO)Br_3(Et_2S)(Et_2SO)$*		1830 ν(NO) 920 ν(SO)	
$Os(NO)Cl_2(Et_2PPh)_2(MET)$*		1800 ν(NO) 1090 ν(CO)	

KEY

MET = 2-methoxyethanoate (M) = multiplet (Q) = quintet
* Structure of these complexes determined by full single crystal X-ray analysis.

TABLE 4.1

Summary of analytical and spectroscopic data

CHAPTER 5

THE REACTION AND PHOTO- CHEMISTRY OF RHODIUM AND IRIDIUM ORGANOPHOSPHINE AND ORGANOSULPHIDE COMPLEXES

5.1 INTRODUCTION

In this Chapter the photochemistry of the five coordinate complexes of the type $M(NO)X_2(PPh_3)_2$ for M = Rh, Ir; X = Cl, Br, I is described. The preparation of rhodium complexes of the type $Rh(NO)X_3(PPh_3)_2$ and $Rh(NO)X_n(Et_2S)_2$ was investigated and is also described.

5.2 THE PHOTOCHEMISTRY OF DIHALOGENO(NITROSYL)-BIS(TRIPHENYLPHOSPHINE)RHODIUM(III) COMPLEXES

$Rh(NO)X_2(PPh_3)_2$ X = Cl, Br, I.

5.2.1 Introduction

Complexes of the stoichiometric type $Rh(NO)X_2L_2$ for L = PPh_3 are well characterisd [Kukushkin & Danilina 1972; Kukushkin & Danilina 1974; Aharmad et al. 1974c; Caulton 1974; Dolcetti et al. 1972; Goldberg et al. 1975; Hieber & Heinicke 1962; Kukushkin & Danilina 1975; Miki et al. 1975; Robinson & Uttley 1971; Collman et al. 1969]. The three halogeno- complexes were conveniently prepared using the method of Robinson & Uttley (1971). The bromo- and chloro- complexes are almost insoluble in chloroform but the iodo- complex is sparingly soluble. Using the Varian XL 300 high field n.m.r. spectrometer the ^1H n.m.r. spectra were obtained on the starting materials and the

reaction products. Infrared spectroscopy was also used to follow the reaction.

5.2.2 The Photochemistry of Dihalogeno(nitrosyl)-bis(triphenylphosphine)rhodium(III) complexes

There were no obvious colour changes when solutions of the complexes in reagent grade chloroform were exposed to sunlight. For the bromo- and chloro- complexes it appeared as if the solutions had darkened, but this may have been due to an increase in concentration as a result of the evaporation of some of the solvent.

The solvent was removed under vacuum and the infrared spectra of the solid products showed substantial changes from that of the starting material after a few days exposure to sunlight. In all three cases the nitric oxide ligand appeared to have been lost as there was no evidence for an absorbance attributable to ν(NO) in the infrared spectra of the irradiated complexes. In addition the infrared spectra for all three products showed absorbances at 1120 cm^{-1} and at 1190 cm^{-1}. For the iodo- complex the second absorbance at 1190 cm^{-1} was strong but it was weaker for the bromo- and chloro- complexes. There were also new absorbances in the infrared spectrum for all three products at 540 and 720 cm^{-1} which are diagnostic for the presence of coordinated triphenylphosphineoxide (refer Chapter 4).

For the iodo- complex the ^{1}H n.m.r. spectrum of the irradiation product in chloroform has a strong resonance at δ = 7.52 ppm which is in the correct position for uncoordinated $OPPh_3$. The n.m.r. evidence is less clear for the bromo- and chloro- complexes and the spectra are more complicated suggesting several different phenyl resonances.

The spectral results suggest that one reaction product is a rhodium complex containing coordinated triphenylphosphineoxide, but no nitric oxide. In addition it appears that free triphenylphosphineoxide is produced, particularly for the iodo-complex. The rhodium would be in either the (+I) or (+III) oxidation state since ^{1}H n.m.r. spectra were obtained indicating that the products are diamagnetic. The most likely stoichiometries of the products are $RhX_3(PPh_3)(OPPh_3)$ or four coordinate complexes $RhX(OPPh_3)(PPh_3)_2$. Both these complexes would be diamagnetic. The elemental analytical results for the bromo- and chloro- products are lower than would be expected for a five coordinate complex or for a four coordinate complex. Found (chloro-): C = 51.3%, H = 4.2%; Calculated for $RhCl_3(PPh_3)(OPPh_3)$ $[C_{36}H_{30}Cl_3OP_2Rh]$; C = 57.7%, H = 4.0%; Calculated for $RhCl(OPPh_3)(PPh_3)_2$ $[C_{54}H_{45}ClOP_3Rh]$; C = 68.9%, H = 4.8%. Found (bromo-): C = 45.7%, H = 3.9%; Calculated for $RhBr_3(PPh_3)(OPPh_3)$ $[C_{36}H_{30}Br_3OP_2Rh]$; C = 48.9%, H = 3.4%; Calculated for $RhBr(OPPh_3)(PPh_3)_2$ $[C_{54}H_{45}BrOP_3Rh]$; C = 65.8%, H = 4.6%. It appears that no single pure species was isolated, and these results suggest that the reaction produces a mixture of products. The analytical figures would be lowered for both carbon and hydrogen due to the presence of rhodium halogeno- complexes. Unfortunately the low solubility of the products precluded recrystallisation.

It is an interesting feature of these reactions that the nitric oxide ligand is lost from these complexes during irradiation. Because the NO is lost from the complexes it is likely that either NO (or NO_2) would be the oxidising agent. This is supported by the free ligand studies described in Chapter 4 where it was shown that NO or NO_2 will oxidise triphenylphosphine more rapidly than dioxygen. Unfortunately

the SMS DATA QUAD mass spectrometer was unavailable to analyse the gaseous products of the photochemical reaction and so it was not possible to decide which of the nitrogen oxides was the oxidising agent. If the reaction is similar to those for the ruthenium and osmium complexes, then NO is probably the oxidising agent. Since all the NO is lost from the complexes there would be plenty of free NO available, and as described in Chapter 4 little nitric oxide is required to bring about the oxidation.

5.3 AN INVESTIGATION OF THE PREPARATION OF TRIHALOGENO(NITROSYL)BIS(TRIPHENYLPHOSPHINE) RHODIUM COMPLEXES $Rh(NO)X_3(PPh_3)_2$ for X = Cl, Br

Complexes of the form $Rh(NO)X_3L_2$ for X = halogen, L = tertiaryphosphine have been reported [Baird 1971; Kukushkin & Singh 1970; Pandey & Argarwala 1980a] but attempts in this work to prepare the complexes were unsuccessful. Baird (1971) reported the presence of trace amounts of a paramagnetic species during the preparation of $Rh(NO)Cl_2(PPh_3)_2$ from the reaction of the '$Rh(NO)Cl_3$' entity with PPh_3. He investigated this material using E.S.R. spectroscopy, and attributed the E.S.R. spectrum and differing elemental analytical results to the presence of a rhodium(II) complex $Rh(NO)Cl_3(PPh_3)_2$. Baird reported the position of the ν(NO) nitrosyl absorbance in the infrared spectrum as occurring at 1660 cm^{-1}. This is a very low value for a linear NO^+ ligand and as discussed in Chapter 2 is more typical for bent NO^-. Haymore and Ibers (1974) have prepared the iridium analogue $Ir(NO)Cl_3(PPh_3)_2$ and found the ν(NO) absorbance to occur at 1732 cm^{-1} a more reasonable value for NO^+.

Pandey and Argarwala (1980a) reported the preparation of $Rh(NO)X_3(PPh_3)_2$ and $Rh(NO)X_2(PPh_3)_2$ for X = Cl, Br by the reaction of NOX with $RhCl(PPh_3)_3$. Although analytical results were reported for almost all of the elements present, the identity of some of these products remains uncertain. The spectral results given by Pandey and Agarwala (1980a) do not agree with previously reported spectral data. For example they report the position of the ν(NO) absorbance in the infrared spectrum of the complex $Rh(NO)Cl_2(PPh_3)_2$ as occurring at 1390 cm^{-1} which is significantly lower than the value of 1630 cm^{-1} reported by others [Baird 1971; Robinson & Uttley 1971] and found in this work.

Pandey and Agarwala studied the complexes obtained using E.S.R. spectroscopy and detected a paramagnetic species, which they attributed to complexes of the type $Rh(NO)X_3(PPh_3)_2$. From these results, and the low value of the ν(NO) absorbance, they assigned an oxidation state of four to the rhodium, which seems unlikely.

Kukushkin and Singh (1970) report the formation of the complexes $Rh(NO)X_3(PPh_3)_2$ for X = Cl, Br by two different methods. The first method involved the treatment of the complex $Rh(NO)X(PPh_3)_2$ with Cl_2 or Br_2. The other method involved the addition of nitric oxide gas to a carbonyl analogue $Rh(CO)X_3(PPh_3)_2$. There is some doubt over the composition of their products as the authors only carrried out nitrogen and rhodium analysis. The results they obtained are in good agreement with the calculated values for the trihalides, but do not differ significantly from the values calculated for the dihalides as can be seen from Table 5.1.

Compound	Rh %	N%
$Rh(NO)Cl_3(PPh_3)_2$ §	13.50	1.83
$Rh(NO)Cl_2(PPh_3)_2$ §	14.13	1.90
$Rh(NO)Cl_3(PPh_3)_2$ †	13.47	2.01
$Rh(NO)Br_3(PPh_3)_2$ §	11.47	1.65
$Rh(NO)Br_2(PPh_3)_2$ §	12.59	1.71
$Rh(NO)Br_3(PPh_3)_2$ †	11.75	1.72

KEY

(§) = calculated value
(†) = experimental value found by Kukushkin & Singh (1970).

TABLE 5.1

Summary of analytical data for complexes of the type $Rh(NO)X_n(PPh_3)_2$

In contrast to Baird (1971), and Pandey and Agarwala (1980a), Kukushkin and Singh (1970), propose that the rhodium is in the tervalent oxidation state. The nitrosyl absorbances reported of ca. 1630 cm^{-1} (depending on the halogen present) are similar in position to that reported for the dihalide complexes $Rh(NO)X_2(PPh_3)_2$ and it is possible that this is what is has been formed.

In this work the methods of Baird (1971), and Kukushkin and Singh (1970) were repeated. In neither case were their products obtained.

The preparation of the chloro- complex using Baird's method yielded the dihalide as was shown by the elemental analysis (see experimental). The product was diamagnetic and the X-ray powder diffraction pattern was similar to that of the ruthenium trichloro- complex $Ru(NO)Cl_3(PPh_3)_2$ (Figures 5.1, 5.2). The single crystal X-ray structure of $Rh(NO)Cl_2(PPh_3)_2$ has been determined [Goldberg et al. 1975] and the coordination geometry around the rhodium is closer to that of a square pyramid than that of a trigonal bypyrimid in agreement with the ^{31}P n.m.r. spectrum [Caulton 1974]. Goldberg et al. (1975) suggest that the molecular packing is determined by the bulky phenyl groups and this may explain the similarity of the powder patterns for the dichloro- and trichloro- complexes found here. Haymore and Ibers (1974) have reported that the iridium analogues $Ir(NO)Cl_3(PPh_3)_2$ and $Ir(NO)Cl_2(PPh_3)_2$ are isostructural.

Similar attempts to prepare the bromo- complex by Baird's method also produced a crystalline material that was found to be diamgnetic. The elemental analytical results of this product gave a good value for carbon but high values for nitrogen and hydrogen for a complex of the stoichiometry $Rh(NO)Br_3(PPh_3)_2$. Found: C = 48.3%, H = 4.3%, N = 3.1%; Calculated for $Rh(NO)Br_3(PPh_3)_2$ [$C_{36}H_{30}Br_3NOP_2Rh$]; C = 48.3%, H = 3.4%, N = 1.6%. The X-ray powder diffraction pattern of the bromo- product was measured and found to be different to that of the chloro- analogue and the ruthenium complex $Ru(NO)Br_3(PPh_3)_2$ (Figure 5.3). The pure dibromo- complex $Rh(NO)Br_2(PPh_3)_2$ was prepared and its X-ray powder diffraction pattern found to be similar to that of the bromo- product (Figure 5.4). The absence of paramagnetism for the bromo- product and the elemental analytical results suggest that the bromo- product is not $Rh(NO)Br_3(PPh_3)_2$, but may be a mixture of

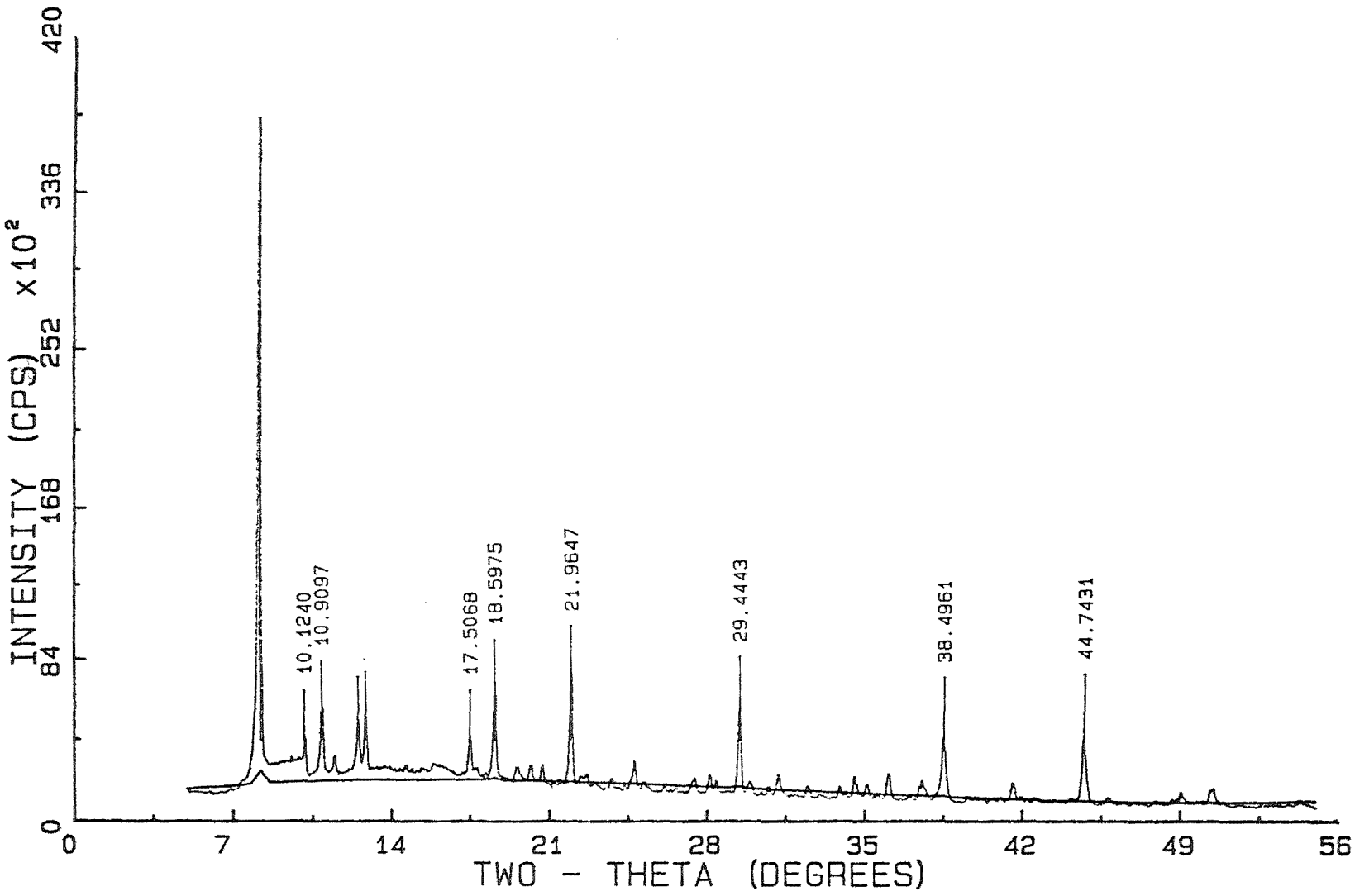


FIGURE 5.1

X-ray powder diffraction pattern for $Ru(NO)Cl_3(PPh_3)_2$

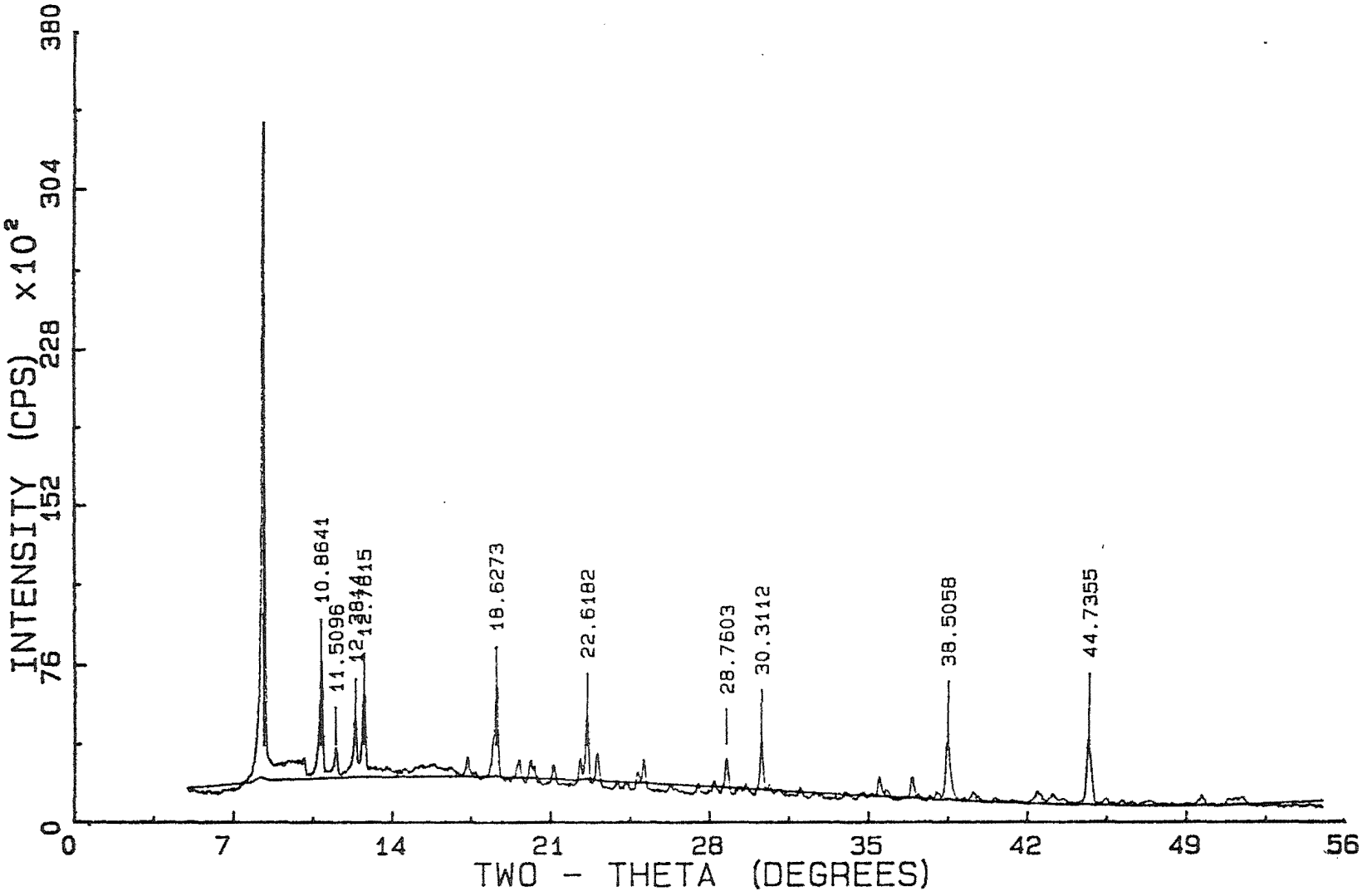


FIGURE 5.2

X-ray powder diffraction pattern for $Rh(NO)Cl_2(PPh_3)_2$

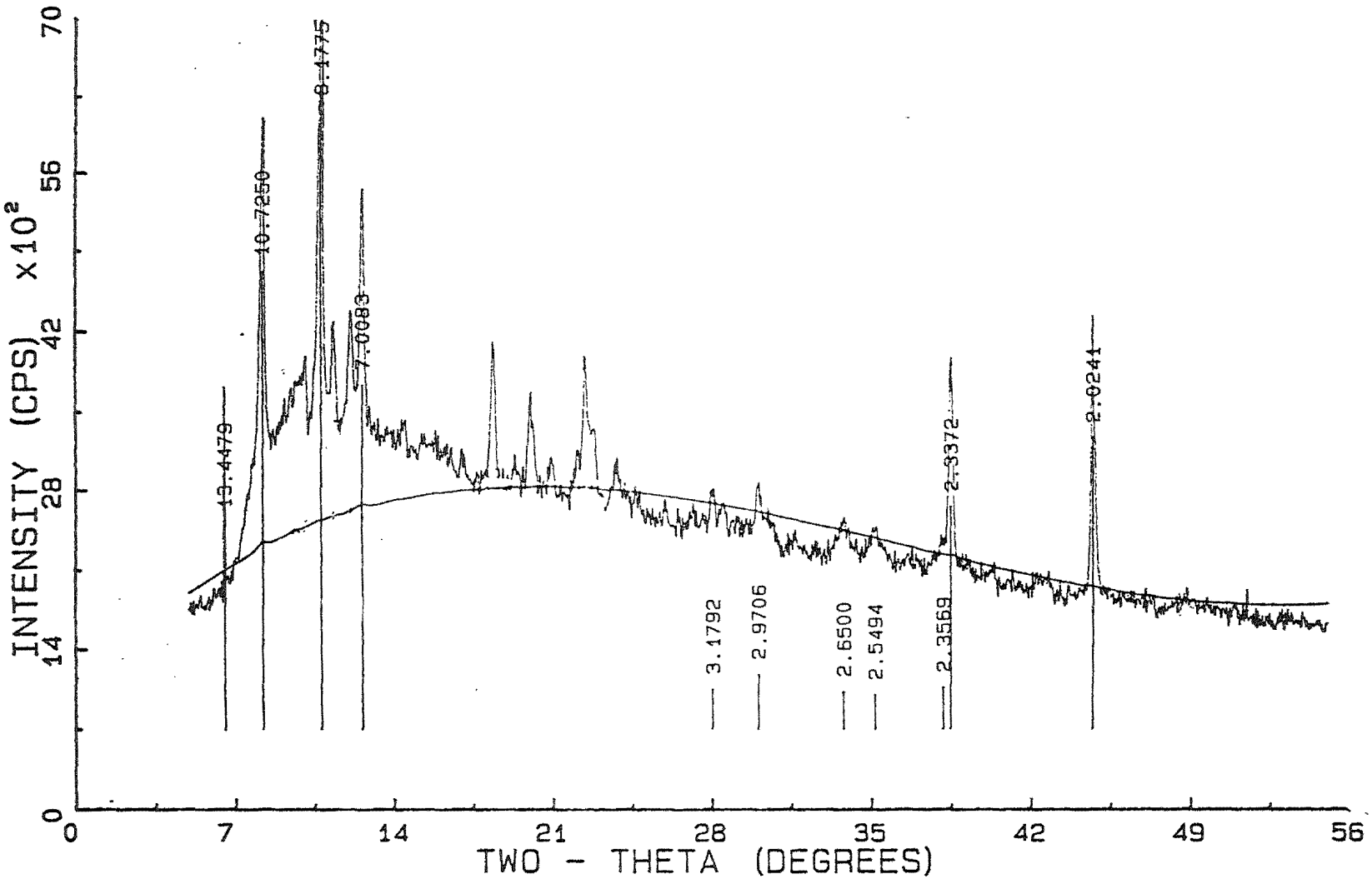


FIGURE 5.3

X-ray powder diffraction pattern for $Rh(NO)Br_n(PPh_3)_2$

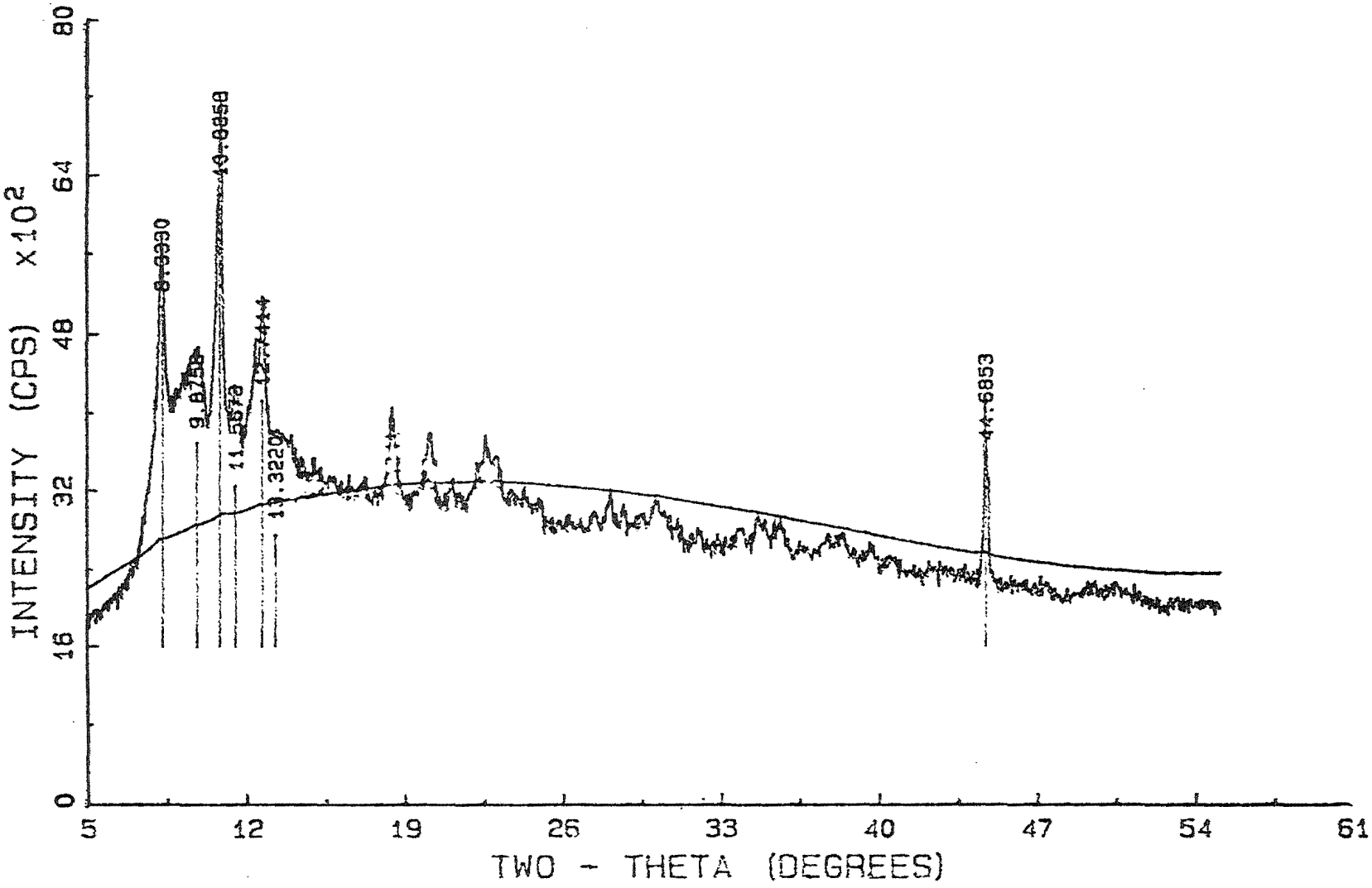


FIGURE 5.4

X-ray powder diffraction pattern for $Rh(NO)Br_2(PPh_3)_2$

$Rh(NO)Br_2(PPh_3)_2$ and some other products e.g. the starting material $RhBr_3 \cdot 3H_2O$.

The method of Kukushkin and Singh (1970) produced some crystalline material, but the products did not show an absorbance attributable to $\nu(NO)$ in the infrared spectrum at the position reported by the authors and the absorbances were broad suggesting that a mixture of compounds had been obtained.

Therefore some doubt remains as to the existence of the trihalogeno- complexes $Rh(NO)X_3(PPh_3)_2$ and it is likely that the authors have produced the dihalogeno- complexes $Rh(NO)X_2(PPh_3)_2$ which was contaminated with some paramagnetic material.

5.4 THE PREPARATION AND REACTION CHEMISTRY OF RHODIUM ORGANOSULPHIDE COMPLEXES

5.4.1 Attempts at the Preparation of Halogeno(nitrosyl)-bis(organosulphide) Complexes of Rhodium

Previous workers in this department have attempted to prepare complexes of the type $Rh(NO)X_n(R_2S)_2$ without success [Page 1978; Teow Sian Keong 1981]. Similar methods were used in this work, but with a variation in the reaction conditions. The first method employed was the same as that used successfully for the preparation of the ruthenium analogues $Ru(NO)X_3(R_2S)_2$ for X = Cl, Br. This involved the treatment of $RuX_3 \cdot 3H_2O$ with nitric oxide gas, removal of the solvent under vacuum, followed by reaction with the appropriate organosulphide. In the preparation of the ruthenium nitrosyl complexes described in Chapter 3, it was found that higher yields

occurred when the starting material $RuX_3 \cdot 3H_2O$ was flushed with nitric oxide gas for long periods of time and then left to stand overnight in a nitric oxide saturated solution before reaction with the organosulphide. The identical method was used with $RhCl_3 \cdot 3H_2O$ as the starting material. Diethylsulphide was added and the solution heated under reflux. The solvent was removed and the final solid product had an infrared spectrum and ^1H n.m.r. spectrum identical with that of the tris-diethylsulphide complex $RhCl_3(Et_2S)_3$ (Table 5.2) [Fergusson et al. 1965]. The procedure was repeated and before adding diethylsulphide, the solvent was removed after addition of the nitric oxide. The infrared spectrum of the oily residue showed no evidence for coordinated nitric oxide even though the solution infrared spectrum before solvent removal had shown an absorbance at 1680 cm^{-1}. The addition of nitric oxide to $RhCl_3 \cdot 3H_2O$ was repeated and the solution heated to drive off any dissolved gas (rather than evaporating to dryness) before addition of Et_2S. When diethylsulphide was added and the solution heated under reflux a brown gas appeared in the condenser suggesting that NO gas was being evolved. The infrared and ^1H n.m.r. spectra of the final product were similar to the tris-diethylsulphide complex. The same procedure was repeated but this time a low mole ratio of diethylsulphide to rhodium was used in order to reduce the likelyhood of the formation of the tris-diethylsulphide complex. However, the tris-diethylsulphide complex appeared to be the only product.

The '$Rh(NO)X_n$' entity was prepared and stirred with Et_2S in EtOH at room temperature overnight. The solution was divided into two, and for one portion the solvent removed under vacuum. For the other the solvent allowed to evaporate at room temperature and pressure under a

stream of N_2. In neither case was crystalline material obtained and the oily residue smelt strongly of Et_2S. Attempts to initiate crystallisation with other solvents were unsuccessful.

The complex $RhCl_3(Et_2S)_3$ was prepared by the reported method [Fergusson et al. 1965] and treated with nitric oxide gas and left overnight in the nitric oxide saturated solution. The solvent was removed and the infrared spectrum of the solid product was identical to that of the starting material and showed no absorbance that could be attributed to $\nu(NO)$.

Reaction of $RhCl_3.3H_2O$ with MNTS and Et_2S in EtOH yielded an orange powder which showed an absorbance in the infrared spectrum at 1160 cm^{-1}. This suggests that a diethylsulphoxide complex was formed.

The addition of diethyltelluride to a solution of the '$Rh(NO)X_n$' entity produced a brown powder. This material showed no evidence for coordinated nitric oxide and the infrared spectrum was similar to that of the tris-diethylsulphide complex $RhCl_3(Et_2S)_3$. However, the absorbances in the infrared spectrum are broad and suggest that a mixture of compounds was produced. Similar attempts using Ph_2S produced no complex containing coordinated nitric oxide.

The addition of EtSPh to a solution of the '$Rh(NO)X_n$' entity produced a light brown powder which showed a broad absorbance in the infrared spectrum at 1610 cm^{-1}. The position of this absorbance suggests that the NO is bound in the bent manner. However, elemental analytical results on this product were not consistent with the expected stoichiometries $Rh(NO)Cl_2(EtSPh)_2$ or $Rh(NO)Cl_3(EtSPh)_2$. Found: C = 34.7%, H = 3.9%, N = 1.1%; Calculated for $Rh(NO)Cl_3(EtSPh)_2$ [$C_{16}H_{20}Cl_3NOS_2Rh$]; C = 37.3%, H = 3.9%, N = 2.7%; Calculated for $Rh(NO)Cl_2(EtSPh)_2$ [$C_{16}H_{20}Cl_2NOS_2Rh$]; C = 40.0%, H = 4.2%, N = 2.9%.

5.4.2 The Oxidation of Diethylsulphide During Preparations of Rhodium Diethylsulphide Complexes

During attempts to prepare $Rh(NO)X_n(Et_2S)$ the oxidation of diethylsulphide occurred often, and this was investigated in greater detail to determine at what stage the oxidation occurred. The complex $RhCl_3 \cdot 3H_2O$ was dissolved in 2-methoxyethanol and flushed with NO gas for four hours and the resulting solution flushed with pure N_2 for 90 minutes. The solution infrared spectrum of this material was found to contain an absorbance at 1680 cm^{-1}. The initial solution changed colour on addition of the NO from a deep red to a lighter red colour and a strong absorbance at 496.6 nm in the UV-visible spectrum disappeared. Diethylsulphide was added and the solution heated under reflux for 15 minutes. A brown gas appeared in the condenser suggesting the evolution of nitric oxide and the solution changed colour from a dark orange to a pale yellow/orange. Removal of the solvent yielded pale orange crystals. The infrared spectrum of this material showed a weak absorbance for $\nu(NO)$ at 1760 cm^{-1} which was not present for the recrystallised product. The infrared spectrum of the recrystallised material was similar to that of the tris-diethylsulphide complex $RhCl_3(Et_2S)_3$ but had two new strong absorbances at 1120 cm^{-1} and at 920 cm^{-1}. It was thought initially that this complex contained two diethylsulphoxide ligands, one sulphur bound and the other oxygen bound to the metal accounting for the two new absorbances in the infrared spectrum. A single crystal X-ray structure analysis was carried out on this compound and is reported in Chapter 7. The analysis found that the stoichiometry was in fact $RhCl_3(Et_2S)_2(Et_2SO)$ and that there were two different molecules in the

asymmetric unit. Both of the diethylsulphoxide ligands are bound through the sulphur, but there is a large difference in the S-O bond lengths in the two separate molecules.

The ^{1}H n.m.r. spectrum of the orange crystals was measured and contained many multiplets. Decoupling experiments were not informative as the resonances were too close to each other to allow independent decoupling. The structure as determined by single crystal X-ray diffraction would have six different environments for the ethyl groupings, but there are more than six sets of triplets and six sets of quartets in the ^{1}H n.m.r. spectrum. One explanation is that the bulk material on which the n.m.r. spectrum was done contains more than one compound. The infrared spectrum can be interpreted on the basis of the crystal structure i.e. two different S-O bond lengths. The elemental analytical results agree with the stoichiometry determined from the X-ray analysis, but there is not much difference between these values and those for other complexes of similar stoichiometry such as bis-diethylsulphoxide complex. Found: C = 28.6%, H = 6.4%; Calculated for $RhCl_3(Et_2S)_2(Et_2SO)$ [$C_{12}H_{30}Cl_3OS_3Rh$]; C = 29.1%, H = 6.1%; Calculated for $RhCl_3(Et_2SO)_2(Et_2S)$ [$C_{12}H_{30}Cl_3O_2S_3Rh$]; C = 28.2%, H = 5.9%.

5.4.3 Discussion

It appears from this study that rhodium will form nitrosyl complexes and organosulphide complexes but will not form complexes with both ligands on the same metal. It is possible that the metal cannot accommodate both the strong π-acceptor NO as well as other π-acceptor ligands such as the organosulphides. However, nitrosyl

organophosphine complexes exist, and the organophosphines are probably better π-acceptors than organosulphides. It is possible that in this case the low solubility of the phosphines may be the stabilising factor in their formation. The fact that nitric oxide appears to be more labile than alkyl- and arylsulphide ligands may mean that there is little metal to ligand π-interaction with rhodium in this oxidation state. Hence the principal stabilising influence may be the σ-donating ability of the ligand rather than the metal to ligand π-interaction.

The overall driving force for the reaction seems to be the formation of the tris-sulphide complex. It seems that the nitric oxide is unable to replace a diethylsulphide ligand in this complex, perhaps because it would lead to an unfavourable oxidation state for the rhodium.

5.5 THE PHOTOCHEMISTRY OF DIHALOGENO(NITROSYL)-BIS(TRIPHENYLPHOSPHINE)IRIDIUM(III) COMPLEXES $Ir(NO)X_2(PPh_3)_2$ X = Cl, Br, I.

5.5.1 Introduction

The dihalide complexes of the stoichiometric type $Ir(NO)X_2(PPh_3)_2$ for X = Cl, Br, I were prepared by the method of Robinson & Uttley (1971). The X-ray structure has been determined for the complex $Ir(NO)Cl_2(PPh_3)_2$, and it is isostructural with the rhodium analogue [Mingos & Ibers 1971b]. The trihalogeno- complexes are known and are better characterised for iridium than for rhodium [Haymore & Ibers 1974; Malatesta et al. 1963; Angoletta et al. 1982].

5.5.2 The Photochemistry of Dihalogeno(nitrosyl)-bis(triphenylphosphine)iridium(III) Complexes

The iridium complexes like the rhodium analogues are not very soluble in chloroform. The iodo- complex is more soluble forming a dark red-brown solution whereas the bromo- and chloro- complexes form pale orange suspensions. There was no obvious changes when a suspension of the chloro- complex in chloroform was exposed to sunlight. The pale orange suspension of the bromo- complex went into solution forming an light orange solution and the iodo- complex gave no obvious colour change when exposed to sunlight but the colour was intense to begin with.

After irradiation the solvent was removed under vacuum and the infrared spectra measured on the solid products. The infrared spectra showed that the nitric oxide ligand had been lost from the starting material for all three halogeno- complexes after short exposure times (1-2 days). There was clear evidence, for all three complexes, of absorbances in the infrared spectra at 1120 cm^{-1} and 1180 cm^{-1} and there were also new absorbances at 540 and 720 cm^{-1} which suggests the presence of coordinated triphenylphosphineoxide. The solid products were dissolved in deuterated chloroform and the ^{1}H n.m.r. spectra measured. For all three halogeno- complexes there was evidence from the phenyl resonances for uncoordinated triphenylphosphineoxide in addition to another set of resonances at a different position to that of the starting material.

The spectral evidence indicates the formation of coordinated triphenylphosphineoxide complexes as well as free triphenylphosphineoxide. This is similar to the situation found for

the ruthenium, osmium and rhodium complexes. The rhodium and iridium complexes are similar in their photochemical behaviour, both losing the nitric oxide ligand easily. The mass spectrometer was unavailable to measure the gaseous reaction products, but as discussed for the rhodium complexes it would seem reasonable that either NO or NO_2 would be the oxidising agent.

5.6 EXPERIMENTAL

The elemental analytical results and spectroscopic data are summarised in Table 5.2 at the end of the experimental section.

5.6.1 Preparation of the Ligands and Reagents

a) Organophosphines and organochalcogens

Triphenylphosphine (Aldrich), triphenylphosphineoxide (Aldrich), diethylsulphide (Koch Light), and diethyltelluride (Strem) were obtained commercially and used without furthur purification. Ethylphenylsulphide and diphenylsulphide were prepared as outlined in Chapter 3.

b) MNTS N-methyl N-nitroso p-toluenesulphonamide

This reagent was puchased commercially (Alrich) and used without furthur purification. Attempts to purify an old sample of MNTS by recrystallising from benzene [Perrin et al. 1980] were unsuccessful and reactions carried out using this material did not give the required products. Fresh samples of MNTS gave excellent results and this highlights the importance of correct storage of air and moisture sensitive materials. The new sample was stored in the dark in a desiccator over phosphorus pentoxide.

c) Nitric oxide

Nitric oxide was prepared as outlined in Chapter 3.

5.6.2 Preparation of the Complexes

a) Trichlororhodium(III) trihydrate $RhCl_3 \cdot 3H_2O$

The complex $RhCl_3 \cdot 3H_2O$ was obtained commercially (Alfa) and used without furthur purification.

b) Tribromorhodium(III) trihydrate $RhBr_3 \cdot 3H_2O$

The complex $RhCl_3 \cdot 3H_2O$ (0.25g) was dissolved in 47% HBr (10-15ml) and heated to dryness gently on a water bath three times.

c) Dihalogeno(nitrosyl)bis(triphenylphosphine)rhodium(III)

$Rh(NO)X_2(PPh_3)_2$ X = Cl, Br, I.

The bromo- and chloro- complexes were prepared by the method of Baird (1971) and the iodo- complex by the method of Robinson and Uttley (1971). The chloro- complex was prepared by heating under reflux an ethanol solution (30ml) of PPh_3 (0.3g) and the '$Rh(NO)Cl_n$' entity (prepared by treating 0.15g of $RhCl_3 \cdot 3H_2O$ with NO gas) for 30 minutes to yield a dark brown microcrystalline material. The bromo-complex was similarly prepared from $RhBr_3 \cdot 3H_2O$ to produce a dark brown microcrystalline material. The iodo- complex was made by heating $RhCl_3 \cdot 3H_2O$ (0.13g) together with lithium iodide (2.0g) in ethanol (20ml) under reflux for 5 minutes and then adding MNTS (0.2g) in ethanol (5ml) and PPh_3 (0.53g) in ethanol (10ml) and heating for a

furthur 30 minutes. A deep burgundy coloured microcrystalline material was obtained.

All the complexes were washed with ethanol, water and methanol before recrystallisation from a CH_2Cl_2/ CH_3OH solvent mixture. If the complex did not crystallise immediately, the solvent was reduced under vacuum and a solution of 0.35g of PPh_3 in 10ml of ethanol was then added.

d) Trichlorotris(diethylsulphide)rhodium(III)

$RhCl_3(Et_2S)_3$

The method of Fergusson et al. (1965) was used, and is similar to that described for the ruthenium analogue described in Chapter 3. There was no intermediate dimeric complex isolated for the rhodium preparation.

e) Trichlorobis(diethylsulphide)(diethylsulphoxide) rhodium(III) $RhCl_3(Et_2S)_2(Et_2SO)$

The complex $RhCl_3 \cdot 3H_2O$ (0.15g) was dissolved in 2-methoxyethanol and flushed with NO gas for four hours and the resulting solution flushed with pure N_2 for 90 minutes. Diethylsulphide (0.1ml) was added and the solution heated under reflux for 15 minutes. There was evolution of nitric oxide and the solution changed in colour from a dark orange to a pale yellow/orange. The solvent was removed to yield pale orange crystals, which were recrystallised from ethanol. The infrared spectrum of the recrystallised material was similar to that of the tris-diethylsulphide complex but had two new strong absorbances at 1120 cm^{-1} and at 920 cm^{-1}. To obtain better crystals suitable for

X-ray analysis the vapour diffusion technique was used. The complex was dissolved in a small amount of chloroform and the solution placed into a 50ml beaker that had been fixed inside a 600ml beaker. Some hydrocarbon solvent (petroleum ether) was added into the space between the two beakers and a lid placed over the large beaker. The more volatile hydrocarbon solvent diffused into the chloroform and the chunky uneven shaped orange crystals appeared overnight. The product was identified as $RhCl_3(Et_2S)_2(Et_2SO)$ by a single crystal X-ray structure determination (Chapter 7).

f) Chloro(carbonyl)bis(triphenylphosphine)rhodium(I)

$Rh(CO)Cl(PPh_3)_2$

This complex was prepared by the addition of a solution triphenylphosphine (0.6g) in DMF (20ml) to a boiling solution of $RhCl_3.3H_2O$ (0.3g) in DMF (20ml) followed by heating under reflux for 10 minutes. The dark red solution effervesed vigorously and changed to a pale yellow colour. The solution was allowed to cool to room temperature and more PPh_3 added (0.6g in 10ml of DMF). A bright yellow powder precipitated [Grinberg et al. 1968].

g) Trichloro(carbonyl)bis(triphenylphosphine)rhodium(III)

$Rh(CO)Cl_3(PPh_3)_2$

The complex $Rh(CO)Cl(PPh_3)_2$ prepared in (f) (0.67g) was dissolved in $CHCl_3$ (15ml). Chloroform saturated with Cl_2 from a cylinder (Matheson) was added and the solution stirred for 90 minutes at room temperature to yield a yellow solid. This product show an absorbance in the infrared spectrum at 1965 cm^{-1} due to the starting material

which indicated that the reaction was incomplete. Further chloroform saturated with Cl_2 was added and the solution stirred overnight. The infrared spectrum of the product from this reaction showed no evidence of the starting material and the elemental analytical results were consistent with the required stoichiometry [Kukushkin & Singh 1970].

h) Chlorotris(triphenylphosphine)rhodium(I)

$RhCl(PPh_3)_3$

The complex $RhCl_3 \cdot 3H_2O$ (1.0gm) was dissolved in ethanol (35ml) and added to a boiling solution of PPh_3 (6.0g) in ethanol (175ml) and the solution heated under reflux for 30 minutes. The solvent volume was reduced under vacuum and dark burgundy-red crystals of $RhCl(PPh_3)_3$ precipitated in quantitative yield. The complex was washed with diethylether and dried under vacuum [Osborn et al. 1966].

i) Chloro(nitrosyl)bis(triphenylphosphine)rhodium(I)

$Rh(NO)Cl(PPh_3)_2$

The complex $Rh(NO)Cl(PPh_3)_2$ was prepared by treatment of a chloroform solution of $RhCl(PPh_3)_3$ (0.3g in 20ml) with nitric oxide gas for several hours. Ethanol (10ml) and PPh_3 (0.35g) were added to complete precipitation of the complex. Light brown microcrystals were obtained. It is also possible to make this complex from the carbonyl analogue $Rh(CO)Cl(PPh_3)_2$ by treatment with nitric oxide gas [Kukushkin & Singh 1970].

j) Attempts to prepare trihalogeno(nitrosyl)bis(triphenylphosphine) rhodium complexes $Rh(NO)X_3(PPh_3)_2$ for X = Cl, Br.

i) The complex $Rh(NO)Cl(PPh_3)_2$ (0.25g) was dissolved in chloroform (50ml) and a solution of Cl_2 in chloroform (30ml) was added and the mixture stirred for several hours. No precipitation occurred as was reported by Kukushkin and Singh (1970). The solvent was removed under vacuum and there was no colour change in the solid product compared with the starting material. The infrared spectrum of the products did not show an absorbance attributable to ν(NO) at the position reported by the authors.

ii) The complex $Rh(CO)Cl_3(PPh_3)_2$ (0.2g) in dimethylsulphoxide (20ml) was treated with nitric oxide gas for several hours. There was no change in the colour of the complex or in the infrared spectrum. The complex $Rh(CO)Cl_3(PPh_3)_2$ was insoluble in chlorinated solvents used by Kukushkin and Singh (1970) and was only sparingly soluble in dimethylsulphoxide. The authors report the formation of brown microcrystals when $Rh(CO)Cl_3(PPh_3)_2$ is treated with NO.

iii) The complex $RhCl_3 \cdot 3H_2O$ (0.15g) was dissolved in ethanol (40ml) and treated with nitric oxide gas for three hours. Some PPh_3 (0.3g in ethanol 20ml) was added and a pale orange precipitate occurred when the volume of the solvent was reduced. The infrared spectrum showed an absorbance at 1630 cm^{-1} which is the same as that reported for ν(NO) for $Rh(NO)Cl_2(PPh_3)_2$ [Robinson & Uttley 1971]. Magnetic studies indicated that the complex was diamagnetic. Elemental analytical results suggested that the product was the

dihalide. Found: C = 59.8%, H = 4.7%; Calculated for $Rh(NO)Cl_2(PPh_3)_2$ $[C_{36}H_{30}Cl_2NOP_2Rh]$; C = 59.4%, H = 4.2%. The bromo- analogue gave similar results producing a dark brown precipitate, but the elemental analytical results suggested that a mixture of compounds was obtained. Found: C = 48.3%, H = 4.3%, N = 3.1%; Calculated for $Rh(NO)Br_3(PPh_3)_2$ $[C_{36}H_{30}Br_3NOP_2Rh]$; C = 48.2%, H = 3.4%, N = 1.6%.

k) Sodium hexahalogenoiridates(IV)

$Na_2[IrX_6]$ for X = Cl, Br.

These complexes were prepared from the ammonium salts using a cation exchange column by an analogous procedure to that used for the osmium complexes described in Chapter 4.

l) Dihalogeno(nitrosyl)bis(triphenylphosphine)iridium(III)

$Ir(NO)X_2(PPh_3)_2$ for X = Cl, Br, I.

There are several reported methods for the preparation of these complexes [Angoletta & Caglio 1963; Reed & Roper 1969; Boyar et al. 1983; Robinson & Uttley 1971] and the method of Robinson and Uttley (1971) was used. Sodium hexachloroiridate(IV) (0.19g) prepared as in (k) was dissolved in 2-methoxyethanol (10ml) and MNTS (0.2g) in 2-methoxyethanol (5ml) were added quickly and successively to a boiling solution of PPh_3 (0.35g) in 2-methoxyethanol (20ml) and the mixture heated under reflux for 30 minutes. The solution was cooled to room temperature and a mustard yellow precipitate was obtained. The bromo- complex was prepared similarly as a light brown micro crystalline material from sodium hexabromoiridate(IV). The iodo- complex was prepared by refluxing sodium hexachloroiridate(IV) (0.19g)

and lithium iodide (2.0g) in 2-methoxyethanol (30ml) for five minutes and then adding the MNTS and triphenylphosphine as before. When the solution cooled dark red-brown microcrystals precipitated.

The complexes were all washed with ethanol, water and methanol before recrystallising from a CH_2Cl_2/CH_3OH solvent mixture. If any difficulty was encountered in obtaining crystals the solvent volume was reduced and extra triphenylphosphine (0.35g in 10ml of ethanol) was added.

5.6.3 Experimental Conditions for the Photochemical Reactions

The reaction conditions and apparatus used were the same as described in Chapter 3 for the organoselenide complexes.

Compound	Infrared cm^{-1}	Elemental anal. C,H,N Found(Calculated)	^1H n.m.r. (ppm)
$Rh(NO)Cl_2(PPh_3)_2$	1625 ν(NO)	59.8(59.4), 4.7(4.2) 1.7(1.9)	
$Rh(NO)Br_2(PPh_3)_2$	1640 ν(NO)	52.7(52.9), 4.2(3.7) 1.3(1.7)	
$Rh(NO)I_2(PPh_3)_2$	1625 ν(NO)	47.2(47.4), 3.3(3.3)	
$RhCl_3(Et_2S)_3$		30.0(30.0), 6.1(6.3)	1.43(T),3.10(Q)
$RhCl_3(Et_2S)_2(Et_2SO)^*$	1120,920 ν(SO)	28.6(29.1), 6.4(6.1)	
$Rh(CO)Cl(PPh_3)_2$	1965 ν(CO)		7.40(M),7.67(M)
$Rh(CO)Cl_3(PPh_3)_2$	2110 ν(CO)	58.0(58.3), 4.7(4.0), 14.9(14.0)§	
$Rh(NO)Cl(PPh_3)_2$	1630 ν(NO)		
$Ir(NO)Cl_2(PPh_3)_2$	1560 ν(NO)	52.8(52.9), 4.3(3.7)	
$Ir(NO)Br_2(PPh_3)_2$	1560 ν(NO)	48.1(47.7), 3.9(3.3)	
$Ir(NO)I_2(PPh_3)_2$	1560 ν(NO)	42.0(43.2), 3.7(3.0)	

KEY

(*) = characterised by single crystal X-ray diffraction.
(§) = % chlorine.
(M) = multiplet (T) = triplet (Q) = quartet.

TABLE 5.2

Summary of analytical and spectroscopic data

CHAPTER 6

THE PHOTOCHEMISTRY OF SOME PLATINUM METAL TRIPHENYLARSINE AND TRIPHENYLSTIBINE COMPLEXES

6.1 INTRODUCTION

Complexes of the stoichiometric type $Ru(NO)X_3(AsPh_3)_2$ for X = Cl, Br, and $Rh(NO)X_2(AsPh_3)_2$ for X = Cl, Br, and I were prepared and their photochemistry investigated. In addition the ruthenium complex $Ru(NO)Cl_3(SbPh_3)_2$ was made and the photochemistry investigated.

At the end of this chapter a summary of the photochemical reactions for the platinum metal complexes studied in this thesis is given.

6.2 FREE LIGAND STUDIES

The ligands $AsPh_3$ and $SbPh_3$ were investigated to see if they could be oxidised as had been observed for the organophosphine and organosulphide ligands. The ligands were dissolved in reagent grade chloroform and treated with NO, O_2, or a mixture of gases. After reaction the solvent was removed under vacuum and the solid products investigated using infrared spectroscopy and ^1H n.m.r. spectroscopy. In both cases a reaction was found to occur with a mixture of the gases NO and O_2. Triphenylarsine was readily oxidised by the mixture of gases to give a product that showed a large broad absorbance in the infrared spectrum at 880 cm^{-1}. This is a similar region reported for the absorbance of triphenylarsineoxide (880 - 890 cm^{-1}) [Smith 1973; Rodley et al. 1965]. There were also absorbances at 1350 and 1665

cm^{-1} which has been reported as arising from addition compounds of the form $R_3AsO.N_2O_4$ [Smith 1973]. The ^1H n.m.r. spectrum showed a resonance at δ = 7.60 ppm which is consistent with that reported for $OAsPh_3$ [Smith 1973]. There was no evidence for reaction with dioxygen and UV-radiation in chloroform even after several hours of irradiation. The addition of a trace amount of the ruthenium complex $Ru(NO)Br_3(AsPh_3)_2$ to this mixture did not act as a catalyst for any oxidation reaction.

Unlike triphenylarsine, triphenylstibine did not react with the NO/O_2 mixture, but did react with O_2 in the presence of UV-radiation after a long period (4 hours) of irradiation. The infrared spectrum of the product showed a strong broad absorbance at 660 cm^{-1} which is characteristic of triphenylstibineoxide [Smith 1973].

6.3 THE PHOTOCHEMISTRY OF RUTHENIUM TRIPHENYLARSINE AND TRIPHENYLSTIBINE COMPLEXES

6.3.1 The Photochemistry of Trihalogeno(nitrosyl)-bis(triphenylarsine)ruthenium(II) Complexes $Ru(NO)X_3(AsPh_3)_2$ X = Cl, Br.

The complexes $Ru(NO)X_3(AsPh_3)_2$ for X = Cl, Br were conveniently prepared by the method of Robinson and Uttley (1971). The bromo-complex required several recrystallisations before it was pure enough to use. Attempts to prepare the iodo- analogue by this method were unsuccessful.

Both complexes were sparingly soluble in chloroform. Nonetheless ^1H n.m.r. spectra were obtained using the Varian XL 300 high field instrument.

There were no obvious colour changes when chloroform suspensions of the complexes were exposed to sunlight. The solvent was removed under vacuum and the solid products analysed using ^1H n.m.r. and infrared spectroscopy. The infrared spectra showed new absorbances in the correct region for ν(AsO) for both the complexes; 850 cm^{-1} [Poddar et al. 1974; Natarajan et al. 1976a; Rodley et al. 1965; Smith 1973]. There is little evidence for the metal oxygen stretch; ν(RuO) = 460 cm^{-1} [Rodley et al. 1965; Natarajan et al. 1976a] but this is more difficult to observe because there are other absorbances in this region. However, there is a definite broadening in this region. The ^1H n.m.r. spectra gave evidence for the presence of free triphenylarsineoxide (δ = 7.60 ppm) for both complexes. In addition the ^1H n.m.r. spectra for both complexes has new resonances in the phenyl region attributable to the formation of a new complex containing coordinated triphenylphosphineoxide, along with a reduction in the intensity of the resonances due to the starting material. The infrared spectra for the bromo- complex is shown in Figures 6.1 and 6.2 and the ^1H n.m.r. spectrum in Figure 6.3.

Like the ruthenium organophosphine and organosulphide complexes there is little evidence in the infrared spectra for the loss of nitric oxide. Based on the free ligand studies it would seem reasonable to suggest that nitric oxide plus dioxygen are the oxidising agents. Poddar et al. (1974) reported the formation of $RuCl_3(AsPh_3)_2(OAsPh_3)$ from the reaction of O_2 with $RuCl_3(AsPh_3)_3$. This was in contrast with earlier reports of the formation of dioxygen

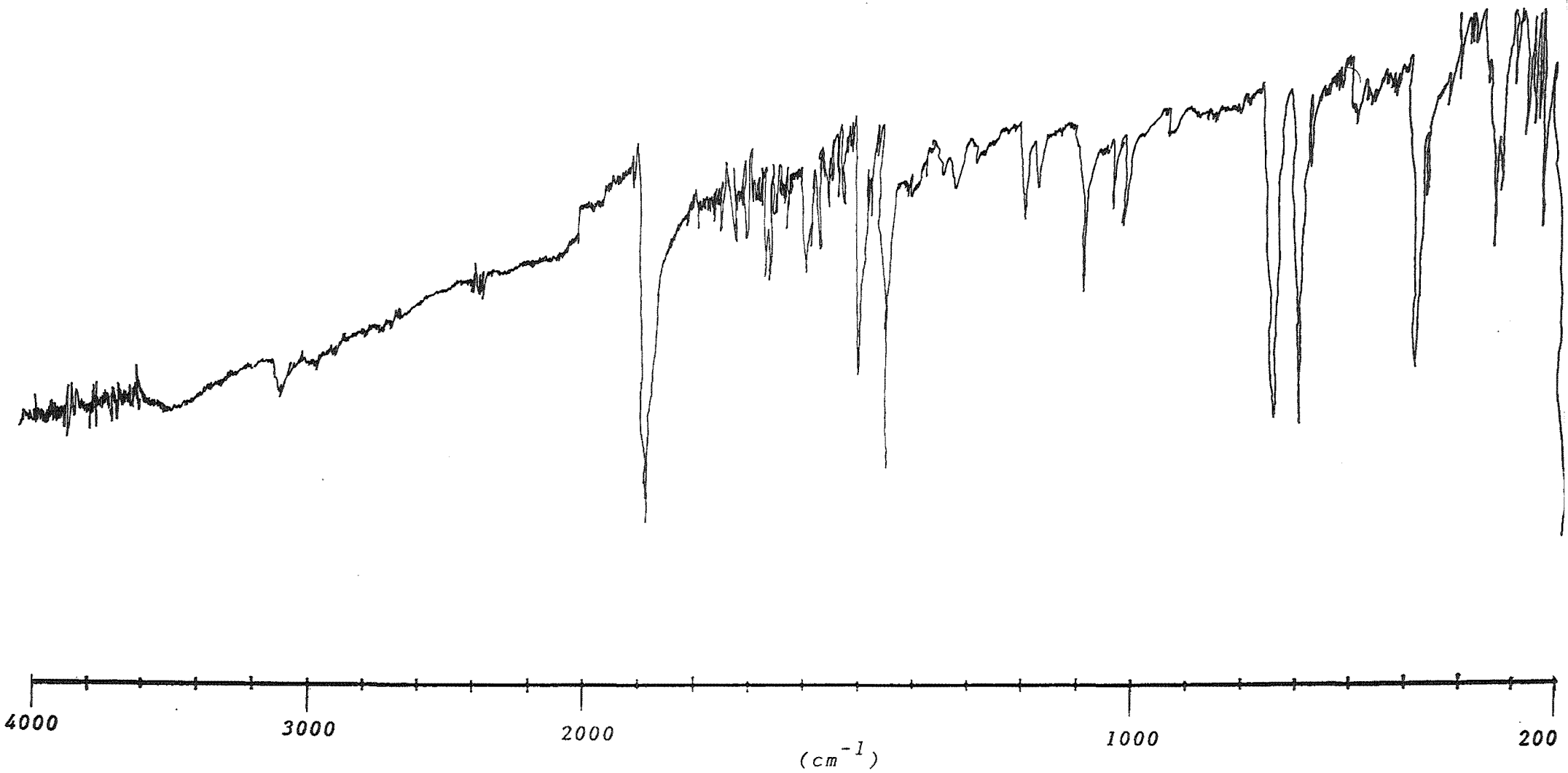


FIGURE 6.1

Infrared spectrum for $Ru(NO)Br_3(AsPh_3)_2$

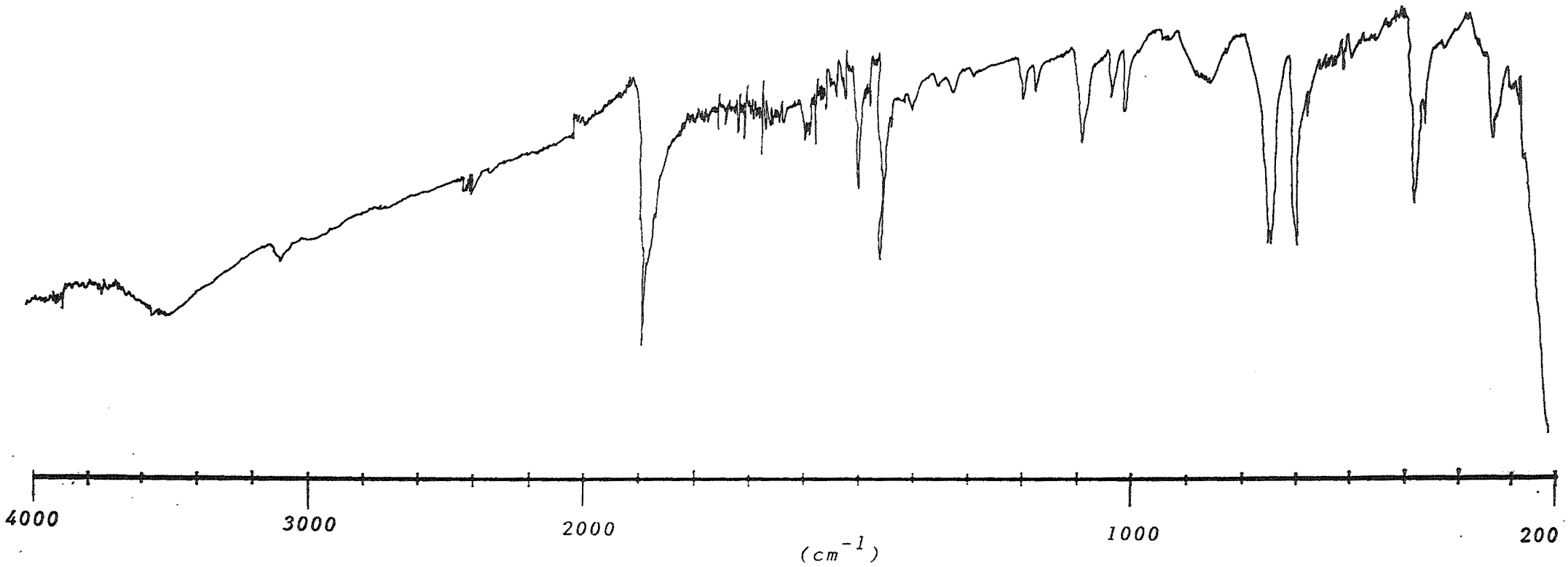
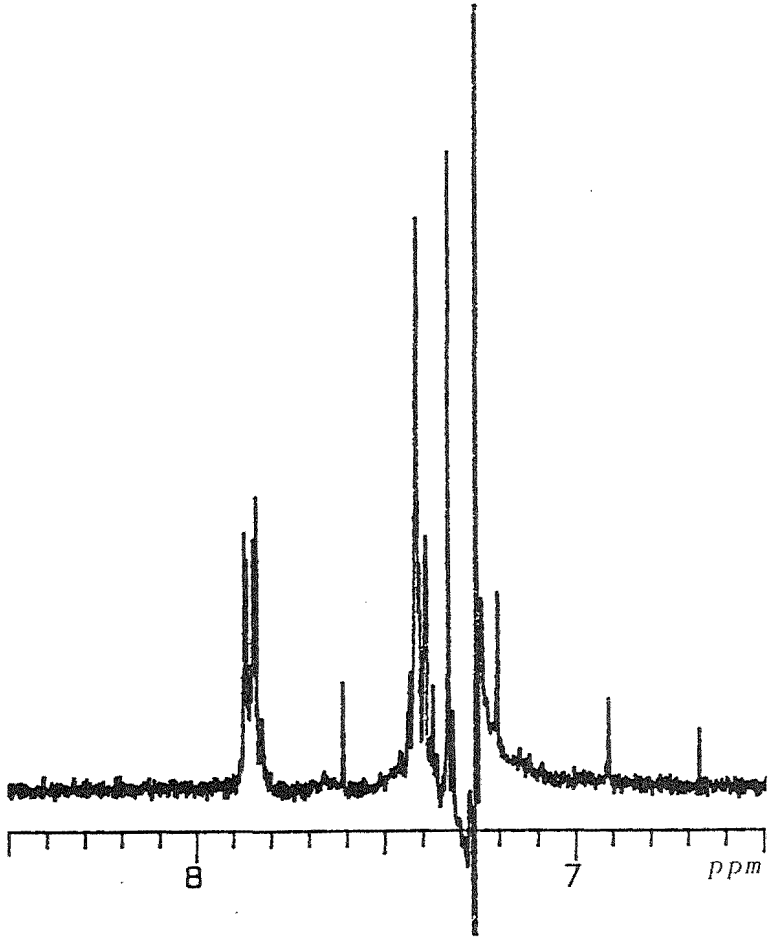
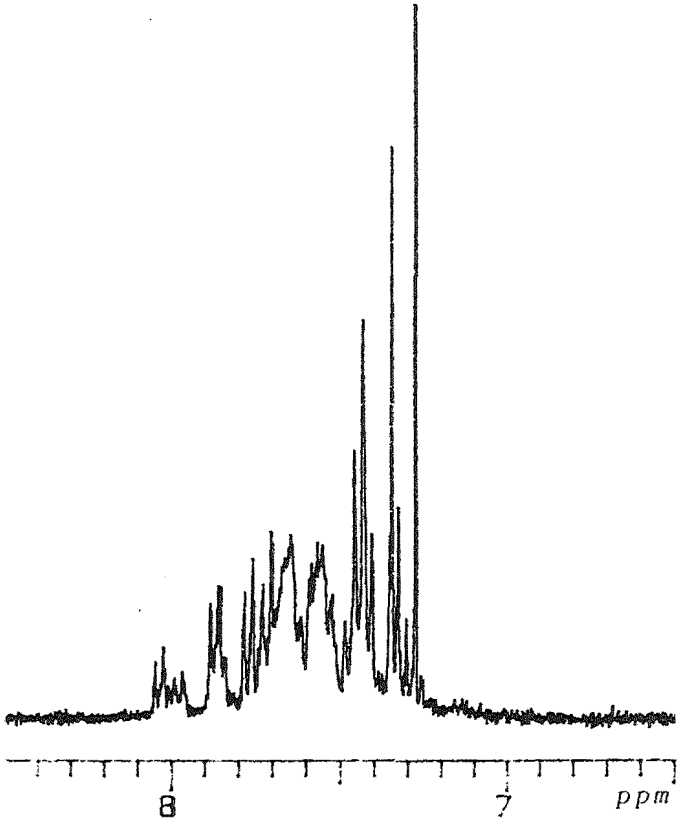


FIGURE 6.2

Infrared spectrum for $Ru(NO)Br_3(AsPh_3)_2$ after irradiation



(A) before irradiation



(B) after irradiation

FIGURE 6.3

^{1}H n.m.r. spectrum for $Ru(NO)Br_3(AsPh_3)_2$

adducts [Taqui Khan et al. 1971]. It would appear that in this case dioxygen is the oxidising agent. The solvent employed was benzene and they claimed that triphenylarsineoxide was formed when $RuCl_3(AsPh_3)_3$ was heated under reflux with O_2 or just had O_2 bubbled through a solution at room temperature. It is possible that the ruthenium complex may act as a catalyst, or that the oxidation of triphenylarsine by dioxygen would proceed in benzene. However, as indicated above the addition of trace amounts of the ruthenium complex $Ru(NO)Br_3(AsPh_3)$ in chloroform did not aid in the oxidation of triphenylarsine by dioxygen.

The likely products of the photochemical reaction of $Ru(NO)X_3(AsPh_3)_2$ are complexes of the type $Ru(NO)X_3(AsPh_3)(OAsPh_3)$. The chloro- complex $Ru(NO)Cl_3(AsPh_3)(OAsPh_3)$ has been reported before [Natarajan et al. 1976a]. The authors reported that the complex can be made by the addition of NO to the complex $RuCl_3(AsPh_3)_3$. The infrared spectrum showed an absorbance at 870 cm^{-1} assigned to $\nu(AsO)$ and 1860 cm^{-1} due to $\nu(NO)$. Natarajan et al. (1976a) did not mention whether they observed any absorbance for $\nu(RuO)$. The spectrum reported by Natarajan et al. (1976a) is very similar to that found in this work. There is no evidence for any loss of NO from the complex formed but there is evidence for a broadening in the $\nu(NO)$ absorbance which is expected because the material is likely to be a mixture of the starting material and the complex $Ru(NO)Cl_3(AsPh_3)(OAsPh_3)$.

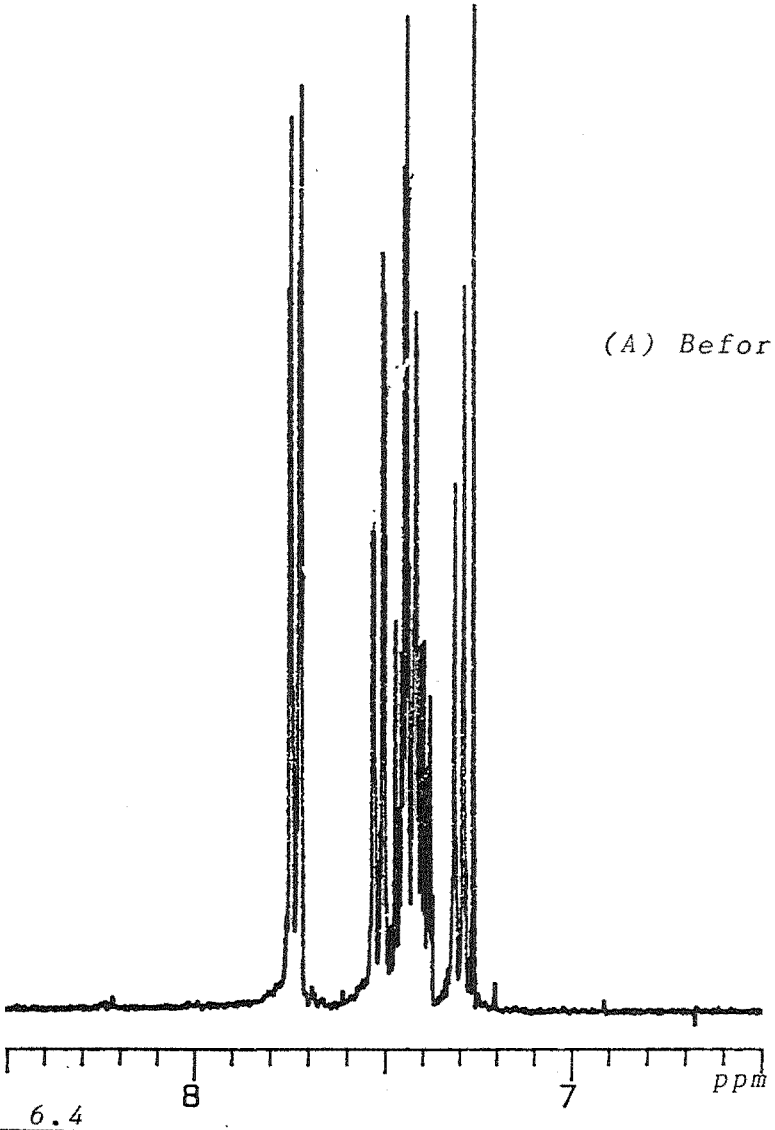
6.3.2 The Photochemistry of Trichloro(nitrosyl)bis(triphenylstibine)ruthenium(II) $Ru(NO)Cl_3(SbPh_3)_2$

This complex was readily soluble in chloroform and there were no obvious colour changes to the solution upon exposue to sunlight. The solvent was removed under vacuum and the solid products investigated using infrared spectroscopy and ^1H n.m.r. spectroscopy. The infrared spectrum of the reaction mixture showed the presence of a new absorbance at 555 cm^{-1} but no evidence for free triphenylstibineoxide (ν(SbO) 660 cm^{-1}).

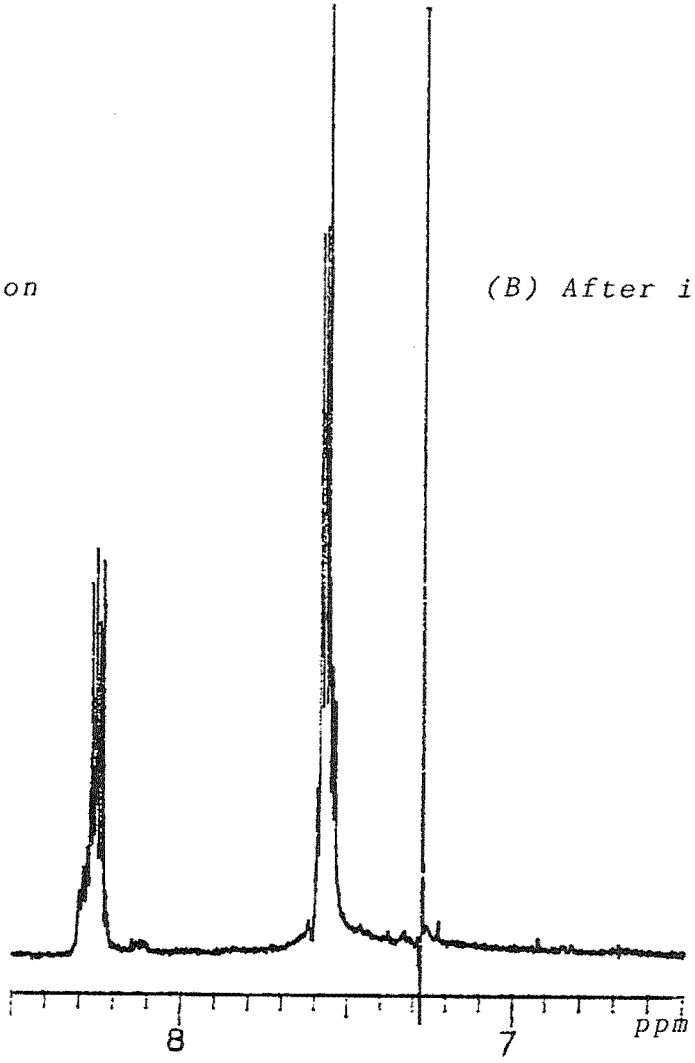
There was no evidence at all for the starting material in the ^1H n.m.r. spectrum. However, there was a new phenyl resonance, significantly down field from the starting material (δ = 7.67 ppm (meta, para); δ = 8.26 ppm (ortho) see Figure 6.4)

The spectra suggests that the reaction product is trans-$[Ru(NO)Cl_3(OSbPh_3)_2]$. The elemental analytical results are in reasonable agreement with this stoichiometry. Found: C = 44.9%, H = 4.8%; Calculated for $Ru(NO)Cl_3(OSbPh_3)_2$ $[C_{36}H_{30}Cl_3NO_3Sb_2Ru]$: C = 44.3%, H = 3.1%. The analytical results are also similar to the calculated values for the starting material $Ru(NO)Br_3(SbPh_3)_2$. Calculated for $Ru(NO)Br_3(SbPh_3)_2$ $[C_{36}H_{30}Cl_3NORu]$: C = 45.8%, H = 3.2%.

The product is likely to be the bis-triphenylarsineoxide and either the trans or cis facial isomer because there appears to be only one magnetic environment for the phenyl group. This is unexpected because the other complexes with oxide ligands have shown a tendency for the oxide to bind opposite the strong π-acceptor NO i.e. leading to the the formation of the cis meridional isomer. However, the



(A) Before irradiation



(B) After irradiation

FIGURE 6.4

^{1}H n.m.r. spectrum for $Ru(NO)Cl_3(SbPh_3)_2$

greater bulk of the triphenylstibine may preclude the formation of the cis meridional isomer. Smith (1973) has reported the absorbance due to ν(SbO) at between 650 - 680 cm^{-1} for the free oxide. It is likely that the position of this absorbance would be shifted to lower frequency upon coordination. There is no evidence in the infrared spectrum for the ν(RuO) absorbance but this is often weak and there are several other strong absorbances in this region of the spectrum which may be obscuring it.

Based on the free ligand studies it is likely that the oxidising agent for the triphenylstibine complex $Ru(NO)Cl_3(SbPh_3)_2$ is O_2.

6.4 THE PHOTOCHEMISTRY OF DIHALOGENO(NITROSYL)-BIS(TRIPHENYLARSINE)RHODIUM(III) COMPLEXES $Rh(NO)X_2(AsPh_3)_2$ X = Cl, Br, I.

Complexes of the stoichiometric type $Rh(NO)X_2(AsPh_3)_2$ for X = Cl, Br, I were made and they were all sparingly soluble in chloroform. There were no obvious physical changes when the suspensions were irradiated. The solvent was removed under vacuum and the solid products investigated using infrared spectroscopy and ^1H n.m.r. spectroscopy.

The infrared spectrum showed dramatic changes with no evidence for ν(NO) in the products. In addition there were new absorbances at; 850 cm^{-1} (chloro-); 845 cm^{-1} (bromo-); and 875 cm^{-1} (iodo-). For the iodo- and chloro- complexes there was also evidence for the presence of uncoordinated triphenylarsineoxide with a broad peak centred around 880 cm^{-1}. There is some evidence for an absorbance at 450 cm^{-1} for the three complexes suggestive of a Rh-O bond. There is increased

broadness in this region but there are several other absorbances which make it difficult to see weak broad absorbances.

The ^{1}H n.m.r. spectra showed a new set of resonances in the phenyl region and also evidence for uncoordinated triphenylarsineoxide for all three complexes.

The spectral evidence suggests that there was a mixture of coordinated and uncoordinated triphenylarsineoxide formed. The products are likely to be of the type $RhX_3(AsPh_3)(OAsPh_3)$, or $RhX(AsPh_3)_2(OAsPPh_3)$ similar to the products obtained when the triphenylphosphine analogues $Rh(NO)X_2(PPh_3)_2$ were photolysed (see Chapter 5). As the irradiation was continued the ^{1}H n.m.r. spectra indicated that the amount of uncoordinated triphenylarsineoxide increased especially for the iodo- complex. The likely oxidisng agents are nitric oxide or a mixture of NO and O_2.

6.5 A SUMMARY OF THE PHOTOCHEMICAL REACTIONS OF PLATINUM METAL COMPLEXES

6.5.1 Introduction

A summary of the photochemical reactions for the platinum metal complexes studied by Page and Teow Sian Keong and studied in this work is given in Table 6.1.

6.5.2 Oxidising Agent

For the organosulphide complexes the oxidising agent was found to be NO_2 as shown by the mass spectrometric results. For the ruthenium triphenylphosphine complexes the mass spectrometric results showed that the oxidising agent was NO. For the other triphenylphosphine and triphenylarsine compexes due to the lack of availabilty of the mass spectrometer it was not possible to decide whether the oxidising agent was NO or NO_2. It is possible that the oxdising agent was O_2 (with radiation), but the results of the free ligand oxidation studies, and the reported oxidation reactions suggest that under the reaction conditions used, NO or NO_2 would be more likely to be the oxidisng agent.

Based on the free ligand studies for triphenylstibine, it appears that O_2 was the oxidisng agent for the ruthenium triphenylstibine complex.

6.5.3 Effect of the Halogen

The main influence of the halogen was seen for the photochemical reactions of the triphenylphosphine and triphenylarsine complexes.

Complex	Product(s)	Oxidising agent(s)	Evidence
$Ru(NO)X_3(R_2S)_2$	$Ru(NO)X_3(R_2S)(R_2SO)$ $[Ru(NO)X_3(Et_2SO)]_2$	NO_2	MS, IFR, N.M.R., UV, EA, XRS
$Ru(NO)X_3(Et_2Se)_2$	$Ru(NO)X_3(Et_2Se)(Et_2SeO)$ §	NO, NO_2	N.M.R., IFR
$Ru(NO)X_3(PPh_3)_2$	$Ru(NO)X_3(PPh_3)(OPPh_3)$ *§	NO	MS, IFR, EA
trans $[Ru(NO)X_3(Et_2PPh)_2]$	cis mer $[Ru(NO)X_3(Et_2PPh)_2]$ §	none	N.M.R., IFR, EA, MS, XRS
$Os(NO)X_3(PPh_3)_2$	$Os(NO)X_3(PPh_3)(OPPh_3)$ *§	NO, NO_2	IFR, N.M.R., EA
$Rh(NO)X_3(PPh_3)_2$	$RhX_3(OPPh_3)(PPh_3)$, $RhX(PPh_3)_2(OPPh_3)$ *	NO, NO_2	IFR, N.M.R.
$Ir(NO)X_3(PPh_3)_2$	$IrX_3(OPPh_3)(PPh_3)$, $IrX(PPh_3)_2(OPPh_3)$ *	NO, NO_2	IFR, N.M.R.
$Ru(NO)X_3(AsPh_3)_2$	$Ru(NO)X_3(AsPh_3)(OAsPh_3)$ *	NO, NO_2	IFR, N.M.R.
$Rh(NO)X_3(AsPh_3)_2$	$RhX_3(AsPh_3)(OAsPh_3)$, $RhX(AsPh_3)_2(OAsPh_3)$ *	NO, NO_2	IFR, N.M.R.
$Ru(NO)Cl_3(SbPh_3)_2$	trans $[Ru(NO)Cl_3(OSbPh_3)_2]$ §	O_2	IFR, N.M.R., EA

TABLE 6.1

Summary of Photochemical Reactions of Platinum Metal Complexes

KEY

XRS	X-ray single crystal structure
*	also some free oxide produced for some halogens
MS	mass spectrometric
EA	elemental analytical results
IFR	infrared spectroscopy
N.M.R.	nuclear magnetic resonance spectroscopy
UV	ultra violet - visible spectroscopy
§	denotes new compound

It appears that for the larger halogens, iodine and bromine, more free triphenylphosphineoxide or triphenylarsineoxide is produced. This may be to the greater steric bulk of the larger ligands resulting in more dissociation of the organic ligands. However, for longer irradiation times there was an increase in the amount of free triphenylphosphineoxide and triphenylarsineoxide produced, and the higher solubilty of the iodo- and bromo- complexes may mean that the reaction has proceeded further.

6.5.4 Effect of the Platinum Metal

The predominant effect seen for the platinum metal was the similarity of the photochemical behaviour of the metal complexes; of ruthenium and osmium, and of rhodium and iridium. Ruthenium and osmium complexes showed evidence for loss of only small quantities of NO whereas the iridium and rhodium complexes readily lost NO. In the complexes studied in this work the NO was bound in the linear fashion for the ruthenium and osmium compexes, and in the bent fashion for the iridium and rhodium compexes. When NO is bound in the linear fashion, there is considerable multiple bonding between the metal and the nitrogen atom. There is less π-interaction for the bent M-NO system and this may explain the greater labilty of NO when it is coordinated in the bent fashion.

6.6 EXPERIMENTAL

The elemental analytical results and spectroscopic data are summarised in Table 6.2 at the end of this section.

6.6.1 Preparation of the Ligands and Reagents

a) Tertiary arsines and stibines

Triphenylarsine, triphenylstibine, methyldiphenylarsine, and triphenylstibine were obtained commercially [Strem] and used without furthur purification. These compounds can be made using a similar method to that used to prepare tertiaryphosphines [Chadaeva et al. 1973].

b) MNTS N-methyl N-nitroso p-toluenesulphonamide

This was obtained commercially [Aldrich] and used without furthur purification.

6.6.2 Preparation of the Complexes

a) Trihalogeno- platinum metal complexes

$MX_3 \cdot 3H_2O$ for M = Rh, Ru; X = Cl, Br.

Trihalogenoruthenium(III) trihydrate $RuX_3 \cdot 3H_2O$ and trihalogenorhodium(III) trihydrate $RhX_3 \cdot 3H_2O$ complexes were obtained as outlined in Chapter 3 and Chapter 5.

b) Trihalogeno(nitrosyl)bis(triphenylarsine)
ruthenium(II) complexes
$Ru(NO)X_3(AsPh_3)_2$ for X = Cl, Br, I.

There are several reported methods for preparing this type of complex [Robinson & Uttley 1972; Natarajan et al. 1976b; Natarajan et al. 1977; Poddar & Agarwala 1973; Stephenson 1968; Stephenson & Wilkinson 1966] and the method of Robinson and Uttley (1972) was used. Trichlororuthenium(III) trihydrate $RuCl_3 \cdot 3H_2O$ (0.13g) in ethanol (10ml) and MNTS (0.2g) in ethanol (5ml) were added quickly and successively to a boiling solution of triphenylarsine (0.61g) in ethanol (20ml) and refluxed for ten minutes. The solution was cooled and khaki microcrystals precipitated. The bromo- analogue (brown microcrystals) was similarly prepared from $RuBr_3 \cdot 3H_2O$. The preparation of the iodo- complex was attempted by metathetical replacement of the chloro- complex. Lithium iodide (2.0g) in ethanol (10ml) and $RuCl_3 \cdot 3H_2O$ (0.13g) were heated under reflux for 5 minutes. To the boiling solution triphenylarsine (0.6g) in ethanol (20ml) and MNTS (0.2g) in ethanol (5ml) were added and the mixture heated for 15 minutes. Dark brown crystals precipitated when the solution was cooled. The elemental analytical results were not consistent with the stoichiometry $Ru(NO)I_3(AsPh_3)_2$. Found: C = 28.6%, H = 2.5%; Calculated for $Ru(NO)I_3(AsPh_3)_2$ [$C_{36}H_{30}As_2I_3NORu$]: C = 38.5%, H = 2.7%.

All complexes were washed with ethanol water and methanol and recrystallised from dichloromethane/methanol.

c) Trichloro(nitrosyl)bis(triphenylstibine)ruthenium(II)

$Ru(NO)Cl_3(SbPh_3)_2$

This complex was prepared in the same way as the triphenylarsine complexes described in (b) yielding a bright orange powder that is readily soluble in chloroform.

d) Dihalogeno(nitrosyl)bis(triphenylarsine)rhodium(III)

$Rh(NO)X_2(AsPh_3)_2$ for X = Cl, Br, I.

There are several reported methods for preparing compounds of this type [Araneo 1966; Araneo & Bianchi 1967; Hieber & Heincke 1961; Robinson & Uttley 1971] and the method of Robinson & Uttley (1971) was used. Trichlororhodium(III) trihydrate $RhCl_3 \cdot 3H_2O$ (0.13g) in 2-methoxyethanol (10ml) and MNTS (0.2g) in 2-methoxyethanol (5ml) were added quickly and successively to a boiling solution of triphenylarsine (0.6g) in 2-methoxyethanol (15ml) and refluxed for 40 minutes. Red-brown microcrystals precipitated when the solution cooled. The bromo- complex (red-brown microcrystals) and iodo- complex (dark brown crystals) were prepared by metathetical replacement in a similar manner to the ruthenium triphenylarsine complexes described in (b) but using 2-methoxyethanol as the solvent. All complexes were washed with ethanol, water, and methanol and recrystallised from dichloromethane-methanol. Both the bromo- and iodo- preparations proved difficult and required several attempts and many recrystallisations before satisfactory elemental analysis figures were obtained. Attempts to prepare a triphenylstibine complex of rhodium by a similar method were unsuccessful, resulting in a product thet showed no evidence for coordinated NO in the infrared spectrum.

6.6.3 Experimental Conditions for the Reactions of the Ligands and the Photochemical Reactions

a) Reaction of the ligands with dioxygen

The reaction conditions and apparatus was as described in Chapter 3 except that the solutions were irradiated for longer periods of time and up to four hours was required for the triphenylstibine.

b) Reaction of the ligands with NO/O_2

The ligand (1gm) was dissolved in reagent grade chloroform and a mixture of NO and O_2 passed through the solution for 5 - 10 minutes and the ligands were left in these solutions for varying periods of time (1 - 2 hours). The solvent was removed under vacuum and the reaction products identified using infrared and ^1H n.m.r. spectroscopy.

c) Photochemical reaction of the complexes

The reaction conditions and apparatus used was the same as that described in Chapter 3 for the organoselenide complexes.

Compound	Infrared cm^{-1}	Elemental anal. C,H Found(Calculated)
$Ru(NO)Cl_3(AsPh_3)_2$	1875 ν(NO)	51.1(50.9), 4.4(3.6)
$Ru(NO)Br_3(AsPh_3)_2$	1860 ν(NO)	44.9(44.0), 4.4(3.1)
$Ru(NO)Cl_3(SbPh_3)_2$	1840 ν(NO)	45.9(45.8), 3.5(3.2)
$Rh(NO)Cl_2(AsPh_3)_2$	1630 ν(NO)	52.6(52.9), 4.0(3.7),
$Rh(NO)Br_2(AsPh_3)_2$	1635 ν(NO)	46.6(47.7), 3.3(3.3)
$Rh(NO)I_2(AsPh_3)_2$	1630 ν(NO)	42.8(43.2), 3.3(3.1)

TABLE 6.2

Summary of analytical and spectroscopic data

CHAPTER 7

THE STRUCTURAL CHEMISTRY OF PLATINUM METAL ORGANOSULPHIDE AND ORGANOPHOSPHINE COMPLEXES

7.1 INTRODUCTION

In this chapter the crystal structures of four new complexes are described. The complexes were isolated during the preparative and photochemical studies of complexes of the general form $M(NO)X_nL_2$. The complexes studied were; $RhCl_3(Et_2S)_2(Et_2SO)$, $Os(NO)Br_3(Et_2S)(Et_2SO)$, $Ru(NO)Br_3(Et_2PPh)_2$, and $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$. The structures were solved using data collected at low temperature except for that of $RhCl_3(Et_2S)_2(Et_2SO)$ which was carried out at room temperature, due to the unavailability of the low temperature apparatus at the time of the data collection. The heavy atom positions were deduced from the Patterson map and the structures solved using the heavy atom method. All structures were corrected for the effects of absorption, and anisotropic thermal parameters were used for the heavy atoms. The structures refined satisfactorily although the structure for $RhCl_3(Et_2S)_2(Et_2SO)$ shows relatively high standard deviations in atom positions and bond lengths due to a lack of data (see Section 7.2). The general techniques used are described in Chapter 11 and the specific details in this chapter.

7.2 THE CRYSTAL AND MOLECULAR STRUCTURE OF TRICHLOROBIS(DIETHYLSULPHIDE)(DIETHYLSULPHOXIDE)-RHODIUM(III) $RhCl_3(Et_2S)_2(Et_2SO)$

7.2.1 Introduction

The complex $RhCl_3(Et_2S)_2(Et_2SO)$ was isolated during attempts to prepare nitrosyl organosulphide complexes for rhodium of the type $Rh(NO)X_n(R_2S)_2$. Evidence from the infrared spectrum suggested that the complex could be a bis-diethylsulphoxide complex, with one sulphur and one oxygen bound diethylsulphoxide ligand. However the structural determination found that there were two different molecules in the asymmetric unit, and that each of these molecules contained only one diethylsulphoxide ligand that was sulphur coordinated. One of the diethylsulphoxide ligands has a short bond between the sulphur and the oxygen atoms and this may explain the difference in the position of the $\nu(SO)$ absorbance. The structure was solved in the triclinic crystal system with space group P1.

7.2.2 Data Collection

A large irregularly shaped red crystal was placed on the diffractometer and centred manually. Refined cell parameters and standard deviations were obtained from the least squares refinement of 25 accurately centred reflections. A triclinic cell was determined and examination of the list of possible unit cell solutions showed no evidence for higher symmetry. Unit cell transformations using the diffractometer software and an independant cell transformation program found no new cells thus confirming the triclinic cell. The mosaicity

of several reflections was checked in different directions through the crystal and the data collection was carried out using the ω-scan technique. Crystal stability was monitored by recording three standard reflections every 100 reflections and no significant variation was observed. The intensities of 1124 reflections were measured. Of these 983 unique reflections were found to have an an intensity greater than 2σ and were used in the structure solution and refinement. No systematic absences were observed and this is consistent with the space groups $P\bar{1}$ and P1.

The crystal data and experimental parameters are summarised in Tables 7.1 and 7.2.

7.2.3 Structure Solution and Refinement

The data was treated for Lorentz and polarisation effects and the structure solution attempted in the centrosymmetric space group $P\bar{1}$. The Patterson map clearly indicated that there was a rhodium atom at the origin. In the space group $P\bar{1}$ the origin is on a centre of inversion and this is inconsistent with the expected structure. It was possible that the molecular structure was different to that indicated by the elemental anaytical results, and the infrared spectrum and so the structure was attempted in the space group P1. However despite numerous attempts no solution was found and so the solution was attempted in the noncentrosymmetric space group P1. The position of the other rhodium atom was deduced from the Patterson map and a Fourier difference map based on the two rhodium atoms revealed the other heavy atoms. The lighter atoms were located from subsequent difference maps.

Formula	$RhCl_3(Et_2S)_2(Et_2SO)$
Formula weight	495.83
Crystal system	triclinic
Space group	P1
a	9.372(4) Å
b	9.608(5) Å
c	12.499(6) Å
α	79.52(4)°
β	86.88(3)°
γ	70.66(3)°
Volume	1040.04(77) $Å^3$
F(000)	508
μ	14.82 cm^{-1}

TABLE 7.1

Crystal data for $RhCl_3(Et_2S)_2(Et_2SO)$

Temperature	298 K
Radiation	Mo K_α (0.71069a)
Bragg angle range	5 - 45°
Scan range	2.4°
Scan speed	fixed 4.88 $^\circ min^{-1}$.
Crystal dimensions	0.40mm x 0.10mm x 0.40mm
Crystal volume	0.0080 mm^3
Calculated density	1.58 g cm^{-3}
Molecules per unit cell	two
Mosaicity	0.25°
Observed reflections	1124
Reflections used in refinement	983
Ratio observations to variables	983:195 (5:1)
Range of transmission factors	0.218 - 0.388

TABLE 7.2

Data Collection parameters for $RhCl_3(Et_2S)_2(Et_2SO)$

The absorption correction was based on ψ-scans and an ellipsoidal model. The two rhodium atoms and the chlorine atoms were assigned anisotropic thermal parameters and the remaining atoms isotropic thermal parameters. No attempt was made to locate the hydrogen atoms. The standard deviations in the atom positions and in the bond lengths and angles are relatively high even though R is acceptable at 0.0588. This is due to the relative paucity of data. The observations to variable ratio is low at approximately five to one. Ideally this should be in the region of ten to one for good standard deviations to be found. Because the space group is P1 there is no symmetry in the structure and there are more variables needed in the structure solution than there would be if the structure were able to be solved in a higher symmetry space group. The data collection was carried out at room temperature and it is possible that a low temperature data collection would be better. Low temperature collections usually give rise to more observed reflections due to the lower amount of thermal vibration of the atoms (see Chapter 11). However, a high percentage of the total number of reflections observed and a low temperature collection may not improve the result significantly. A weighted least squares procedure allowing the weighting parameter to vary was used at the end of the refinement. This led to a final R of 0.0588, a weighted R of 0.0659, and a goodness of fit of 1.006.

Comparison of the observed and and calculated structure factors showed no evidence of extinction. The final electron density difference map showed no anomalies and the residual peaks in the difference map are concentrated around the heavy atoms and are most likely to be associated with anisotropy.

Because the space group P1 is noncentrosymmetric there are two enantiomorphic forms possible for the structure. The correctness of the enantiomorph was checked by inverting the structure (see Chapter 11). The inverted structure gave a significantly lower value for R and was judged to be the correct enantiomorph.

7.2.4 Description of the Structure

The structure consists of two different well separated molecules each with the stoichiometry $RhCl_3(Et_2S)_2(Et_2SO)$. In each molecule three chlorine atoms, two diethylsulphide ligands and the diethylsulphoxide ligand are coordinated to the rhodium in an octahedral arrangement. In both molecules the diethylsulphoxide ligand is sulphur bound. The chlorine atoms are bound in a meridional configuration.

The asymmetric unit is shown in Figure 7.1 and the unit cell packing in Figure 7.2. The atom coordinates and the anisotropic temperature factors are given in Tables 7.3 and 7.4.

7.2.5 Discussion

The rhodium to chlorine bond lengths lie in the range 2.339(11) - 2.370(11) Å similar to other reported bond lengths; 2.331(6) - 2.348(4) Å [Colamarino & Orioli 1976; Rochon et al. 1983; Goldberg et al. 1975; Sokol & Porai-Koshits 1975; Sokol et al. 1975].

The rhodium to sulphur bond lengths for the diethylsulphide ligands are in the range 2.367(11) - 2.402(11) Å which are similar to other reported bond lengths; 2.257(7) - 2.39(2) Å [Colamarino & Orioli

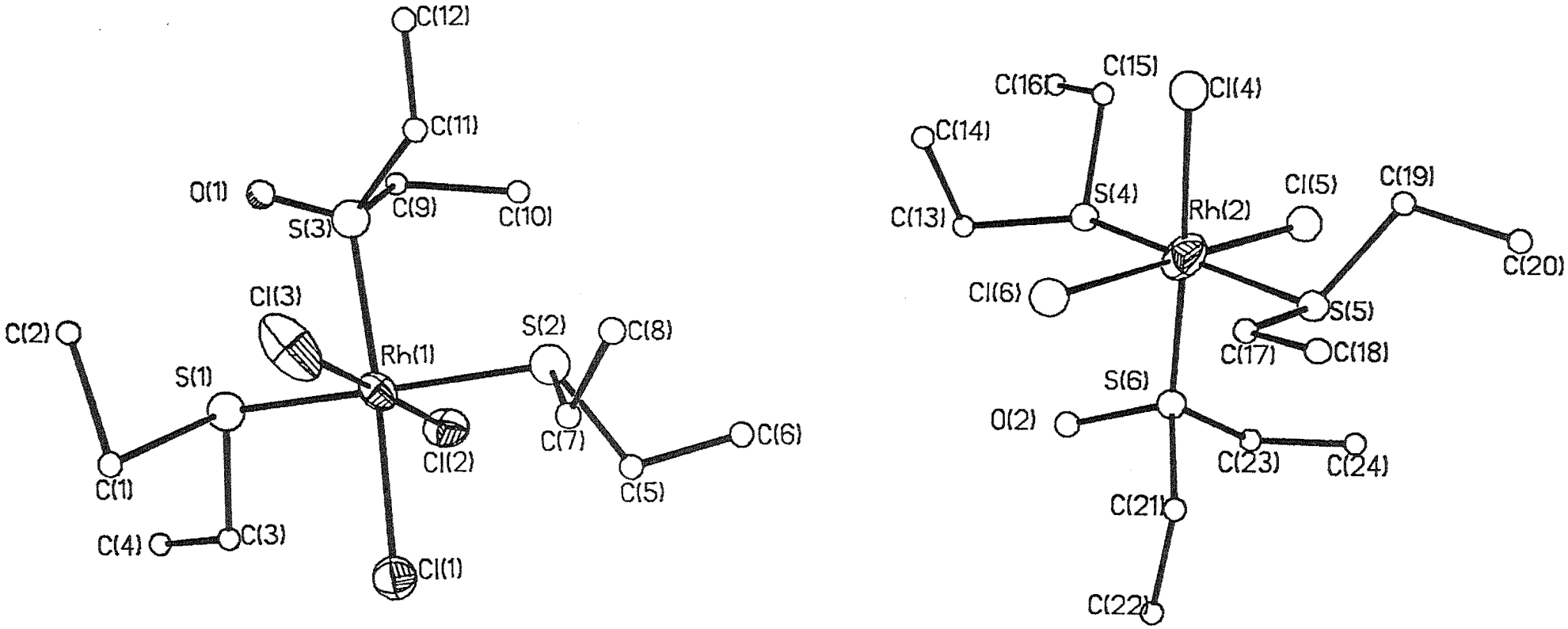


FIGURE 7.1

Perspective view of the structure of $RhCl_3(Et_2S)_2(Et_2SO)$

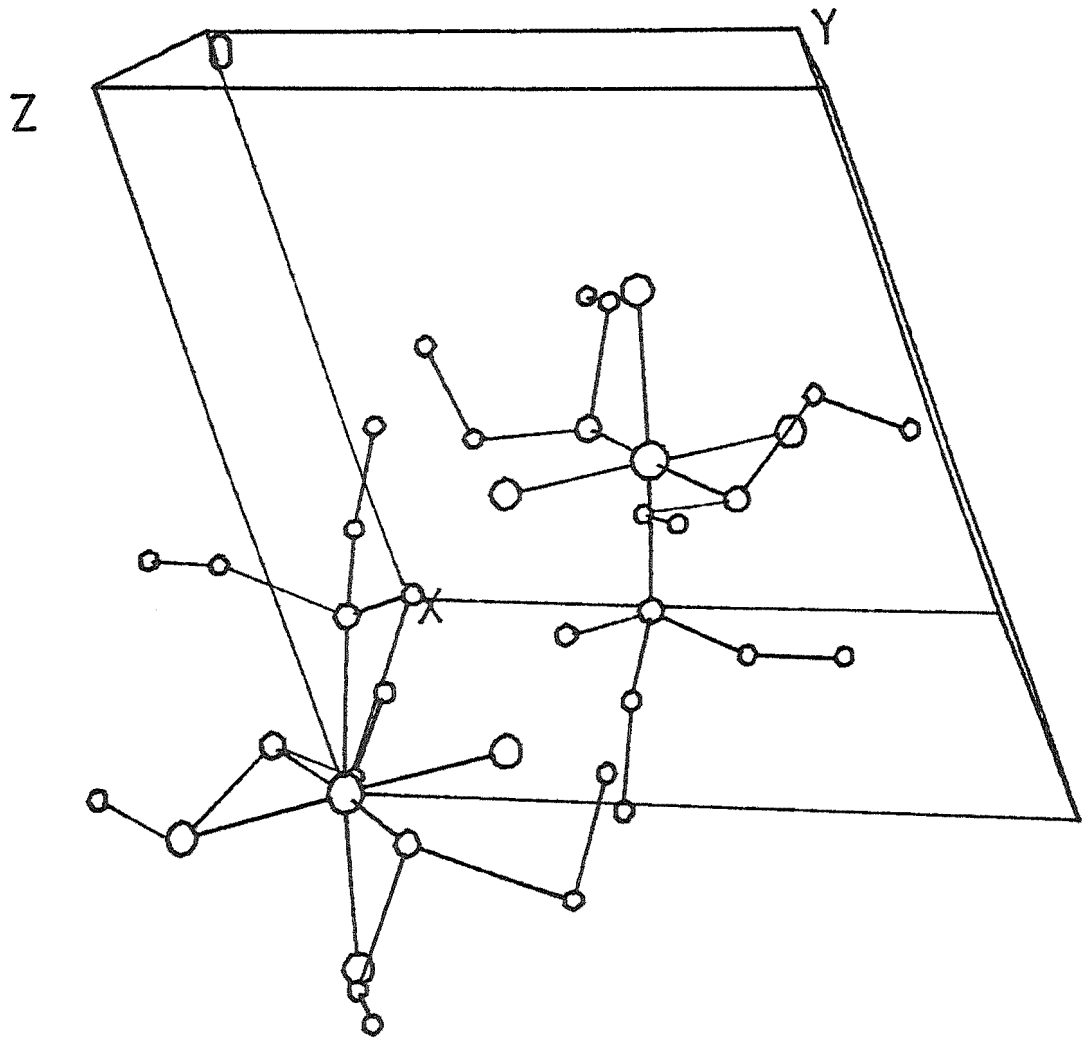


FIGURE 7.2

Unit cell packing for $RhCl_3(Et_2S)_2(Et_2SO)$

Atom	x	y	z	U
Rh(1)	0(1)	0(0)	0(0)	43(1)*
Rh(2)	6241(2)	5499(2)	4909(2)	43(1)*
Cl(1)	2624(8)	9262(8)	9752(7)	41(4)*
Cl(2)	278(11)	7736(11)	1237(10)	44(5)*
Cl(3)	9696(16)	2282(15)	8832(10)	120(19)*
Cl(4)	3596(11)	6211(14)	5177(8)	38(6)*
Cl(5)	5996(13)	7733(10)	3673(9)	93(9)*
Cl(6)	6552(12)	3199(13)	6065(11)	45(5)*
S(1)	89(12)	996(14)	1566(10)	46(1)
S(2)	9884(7)	8768(7)	8521(6)	46(1)
S(3)	7351(10)	982(9)	269(6)	34(2)
S(4)	6113(10)	4553(10)	3271(7)	41(2)
S(5)	6518(12)	6667(12)	6366(10)	57(2)
S(6)	8725(13)	4673(11)	4742(9)	55(2)
O(1)	6938(37)	2100(34)	702(26)	98(8)
O(2)	9357(32)	3080(30)	4194(22)	74(6)
C(1)	878(77)	2943(71)	992(51)	146(16)
C(2)	9208(77)	3784(98)	1240(65)	204(24)
C(3)	1811(38)	9803(37)	2397(29)	49(7)
C(4)	1888(45)	88(41)	3454(30)	85(9)

TABLE 7.3

Atom coordinates (x 10^4) and temperature factors (x 10^3) for $RhCl_3(Et_2S)_2(Et_2SO)$.

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Atom	x	y	z	U
C(5)	1512(42)	6991(44)	8590(32)	69(8)
C(6)	1062(52)	5857(53)	8111(41)	66(9)
C(7)	594(41)	9666(38)	7320(30)	65(7)
C(8)	9922(66)	213(67)	6206(46)	151(16)
C(9)	6370(46)	9693(47)	1229(32)	83(8)
C(10)	6577(37)	8427(35)	350(28)	66(6)
C(11)	6384(37)	1294(34)	9019(28)	39(7)
C(12)	4862(42)	2069(39)	8895(29)	72(7)
C(13)	6274(30)	2651(29)	3482(21)	37(5)
C(14)	4712(44)	2515(39)	3907(31)	76(8)
C(15)	4189(32)	5507(30)	2761(23)	54(6)
C(16)	4393(35)	5064(32)	1456(23)	60(6)
C(17)	6520(67)	5331(67)	7677(51)	121(14)
C(18)	6383(41)	5800(43)	8705(30)	84(8)
C(19)	5324(51)	8462(50)	6076(38)	76(10)
C(20)	5564(72)	9624(78)	6672(58)	109(15)
C(21)	9710(45)	3994(41)	6101(31)	63(9)
C(22)	1582(34)	3272(33)	5721(24)	59(6)
C(23)	9549(35)	5895(33)	3964(25)	60(6)
C(24)	9577(35)	7383(33)	4189(25)	62(7)

TABLE 7.3 CONTINUED

Atom coordinates (x 10^4) and temperature factors (x 10^3) for $RhCl_3(Et_2S)_2(Et_2SO)$.

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh(1)	45(1)	45(2)	47(2)	-2(1)	-5(1)	-23(1)
Rh(2)	41(1)	46(2)	48(1)	-2(1)	1(1)	-28(1)
Cl(1)	41(4)	65(5)	95(7)	-29(6)	7(5)	-15(5)
Cl(2)	44(5)	51(7)	72(8)	5(7)	-16(6)	-8(6)
Cl(3)	125(10)	89(8)	53(7)	47(6)	-25(6)	-88(7)
Cl(4)	38(6)	96(10)	53(8)	5(9)	9(7)	-43(7)
Cl(5)	93(9)	33(6)	51(7)	22(6)	2(7)	-41(6)
Cl(6)	45(6)	43(5)	84(7)	0(0)	0(0)	0(0)

TABLE 7.4

Anisotropic temperature factors ($Å^2 \times 10^3$) for $RhCl_3(Et_2S)_2(Et_2SO)$

1976; Rochon et al. 1983; Sokol & Porai-Koshits 1975; Sokol et al. 1975].

The Rh-S bond lengths for the diethylsulphoxide ligands are 2.209(11) and 2.374(9) Å. The bond length of 2.374(9) Å is similar to that found for the diethylsulphide ligands in this structure and reported in other complexes. However, the bond length of 2.209(11) Å is shorter and may indicate that there is some multiple bonding character between the rhodium and sulphur.

There is a large difference in the S-O bond length for the two diethylsulphoxide molecules. For the diethylsulphoxide attached to Rh(1) the sulphur to oxygen bond length is short at 1.227(34) Å, compared with a S-O bond length of 1.700(31) Å in the other molecule. Other reported S-O bond lengths lie in the range 1.40 - 1.60 Å [Page 1978; Coll et al. 1987b; Fergusson et al. 1976; Sokol & Porai-Koshits 1975]. This suggests that there is multiple bond character between the sulphur and oxygen for the shorter bond length. The Rh-S bond length for this diethylsulphoxide is the longer found in this analysis. The S-O bond length is even shorter than that calculated from the sum of the covalent radii [Ball & Norbury 1974] for triply bonded atoms which would be 1.39 Å. The absorption in the infrared spectrum at 1120 cm^{-1} assigned to ν(SO) for this diethylsulphoxide group lies at the top end of the range for organosulphoxides, but it seems that even allowing for this and the high standard deviation in the bond length that the bond length is anomalously short.

The atom was removed from the structure and a difference Fourier map showed the same position again for the oxygen atom and so it is not possible with the present data set to change this result. It may

be that the lack of data means that this bond length is unreliable except as an indication that it is defintely shorter than normal.

The carbon to sulphur and carbon to carbon bond lengths are similar to reported values: C-S 1.702(41) - 1.796(37) Å; C-C 1.401(56) - 1.485(67) Å [Fergusson et al. 1976; Coll et al. 1987b; Sokol & Porai-Koshits 1975; Sokol et al. 1975].

The bond lengths are given in Table 7.5, and the bond angles in Table 7.6.

Bond	Length	Bond	Length
Rh(1) - S(1)	2.340(14)	Rh(1) - S(2)	2.387(8)
Rh(1) - S(3)	2.375(9)	Rh(1) - Cl(1)	2.343(7)
Rh(1) - Cl(2)	2.370(10)	Rh(1) - Cl(3)	2.339(13)
S(2) - C(7)	1.796(37)	S(3) - O(1)	1.227(34)
S(3) - C(11)	1.771(36)	C(3) - C(4)	1.401(56)
C(11) - C(12)	1.375(46)		
Rh(2) - S(4)	2.402(11)	Rh(2) - S(5)	2.367(13)
Rh(2) - S(6)	2.209(11)	Rh(2) - Cl(4)	2.365(10)
Rh(2) - Cl(5)	2.353(10)	Rh(2) - Cl(6)	2.345(12)
S(4) - C(13)	1.754(30)	S(5) - C(19)	1.702(41)
S(6) - O(2)	1.700(31)	S(6) - C(23)	1.737(36)
C(17) - C(18)	1.418(80)		

TABLE 7.5

Selected bond lengths (Å) for $RhCl_3(Et_2S)_2(Et_2SO)$

Bond	Angle	Bond	Angle
S(1) - Rh(1) - S(2)	174.3(4)	Cl(1) - Rh(1) - S(3)	174.4(3)
Cl(2) - Rh(1) - Cl(3)	177.9(4)	S(3) - Rh(1) - Cl(3)	85.1(4)
Rh(1) - S(3) - O(1)	115.2(18)	Rh(1) - S(3) - C(11)	109.8(11)
Rh(1) - S(2) - C(7)	108.3(14)	S(3) - C(11) - C(12)	122.2(27)
S(2) - C(7) - C(8)	129.2(37)		
S(4) - Rh(2) - S(5)	171.9(4)	Cl(4) - Rh(2) - S(6)	175.7(4)
Cl(5) - Rh(2) - Cl(6)	176.9(4)	Cl(4) - Rh(2) - S(5)	90.8(4)
Cl(4) - Rh(2) - Cl(5)	91.5(4)	Rh(2) - S(6) - O(2)	112.9(13)
Rh(2) - S(6) - C(23)	116.9(10)	Rh(2) - S(5) - C(19)	105.9(18)
Rh(2) - S(4) - C(15)	105.3(10)	Rh(2) - S(4) - C(13)	114.5(10)
C(13) - S(4) - C(15)	103.6(15)		

TABLE 7.6

Selected bond angles (deg) for $RhCl_3(Et_2S)_2(Et_2SO)$

7.3 THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIBROMO(NITROSYL)(DIETHYLSULPHIDE)(DIETHYLSULPHOXIDE)-OSMIUM(II) $Os(NO)Br_3(Et_2S)(Et_2SO)$

7.3.1 Introduction

The complex $Os(NO)Br_3(Et_2S)(Et_2SO)$ was isolated during attempts to produce complexes of the type $Os(NO)X_3(R_2S)_2$ and was found to be isostructural with the ruthenium analogue whose structure has been determined [Coll et al. 1987a].

7.3.2 Data Collection

A bright red coloured thin plate crystal was placed on the diffractometer and centred manually. Refined cell parameters and standard deviations were obtained from the least squares refinement of 25 accurately centred reflections. A monoclinic unit cell determined from precession photography was found and the lattice appeared to be C-centred as was suggested from the preliminary studies. The mosaicity of several reflections was checked in different directions through the crystal and the data collection was carried out using Wycoff-ω scans. Crystal stability was monitored by recording two standard reflections every 100 reflections and no significant variation was observed. A total of 1754 reflections were observed. Inspection of the systematic absences indicated that the likely space groups were Cc or C2/c. However, many attempts to solve the structure in both space groups were unsuccessful and the crystal was remounted and the data collection repeated this time using the ω-scan technique. Several short high speed preliminary data collections were carried out

and it became evident that the C-centring suggested from the photographs was not present and so the data collection was carried out on the basis of a primitive cell. Analysis of the systematic absences showed that the correct space group was $P2_1/c$ and the structure solution was straightforward from this point. For this data collection the intensities of 1965 reflections were measured. Of these 1137 were unique with an intensity greater than 3σ and were used in the structure solution and refinement.

The crystal data and experimental parameters are summarised in Tables 7.7 and 7.8.

7.3.3 Structure Solution and Refinement

The data was treated for Lorentz and polarisation effects and the position of the osmium atom deduced from the Patterson map. Subsequent difference maps showed the remaining heavy atoms and at this stage it was noted that the atom coordinates were similar to the ruthenium analogue. The carbon atom positions from the ruthenium structure were used and allowed to refine.

An absorption correction based on an empirical model was attempted using both thin plate and ellipsoidal models. Of the two models used, the thin plate model produced the better agreement of equivalent reflections than the ellipsoidal model. However a correction based on the Gaussian face indexing procedure was found to produce a better result than either of the empirical models. All the heavy atoms were assigned anisotropic thermal parameters and the lighter atoms isotropic thermal parameters. No attempt was made to locate hydrogen atoms.

Formula	$Os(NO)Br_3(Et_2S)(Et_2SO)$
Formula weight	656.29
Crystal system	monoclinic
Space group	$P2_1/c$
a	13.398(3)Å
b	8.501(2) Å
c	16.199(3) Å
$\alpha = \gamma$	90.000(0)°
β	105.69(1)°
Volume	1776.41(55) $Å^3$
F(000)	1216
μ	140.95 cm^{-1}

TABLE 7.7

Crystal data for $Os(NO)Br_3(Et_2S)(Et_2SO)$

Temperature	163 K
Radiation	Mo K_α (0.71069a)
Bragg angle range	5 - 55^o
Scan range	1.2^o
Scan speed	fixed 4.88 $^o min^{-1}$.
Crystal dimensions	0.20mm x 0.10mm x 0.03mm
Crystal volume	0.0006 mm^3
Calculated density	2.45 g cm^{-3}
Molecules per unit cell	four
Mosaicity	0.28^o
Observed reflections	1965
Reflections used in refinement	1137
Ratio observations to variables	1137:99(11:1)
Range of transmission Factors	0.243 - 0.652

TABLE 7.8

Data collection parameters for $Os(NO)Br_3(Et_2S)(Et_2SO)$

The standard deviations shown indicate that the model is relatively insensitive to changes in the positions of the lighter atoms nitrogen, oxygen and carbon. This is not unexpected since the osmium atom with 76 electrons is a much larger scattering source than the lighter atoms and thus dominates the overall scattering. Some lack of precision in atom positions was noted in the ruthenium structure [Coll et al. 1987a] even though the ruthenium atom is substantially smaller than the osmium. The only bond angle with a large standard deviation is the Os-N-O which is found to be $171.4(29)^{\circ}$ and this is similar to that found in the complex $Ru(NO)Br_3(n\text{-}Pr_2S)_2$ which had an angle of 161.8° and a standard deviation of 2.9° [Coll et al. 1987a]. A weighted least squares procedure allowing the weighting parameter to vary was used at the end of the refinement. This led to a final R of 0.0617, a weighted R of 0.0599, and a goodness of fit of 1.308.

Comparison of the observed and and calculated structure factors showed no evidence of extinction. The final electron density difference map showed no anomalies and the residual peaks in the difference map are concentrated around the heavy atoms and are most likely to be associated with anisotropy.

7.3.4 Description of the Structure

The complex is isostructural with the ruthenium analogue, with three bromine atoms, one diethylsulphide, one diethylsulphoxide and a NO group coordinated to the osmium atom in an octahedral manner. The bromine atoms are coordinated to the osmium in a meridional

configuration, and the diethylsulphoxide ligand is oxygen bound trans to the linear NO group.

The asymmetric unit is shown in Figure 7.3 and the unit cell packing in Figure 7.4. The atom coordinates and the anisotropic temperature factors are given in Tables 7.9 and 7.10.

7.3.5 Discussion

There is little structural data available on osmium complexes of this type to compare the bond lengths obtained in this structure. The bond lengths cited in the text are mainly from organometallic compounds and thus are not directly comparable but serve as a guide.

The diethylsulphoxide ligand is clearly oxygen bound as in the ruthenium structure and the Os-O bond length of 2.074(17) Å is similar to that reported for other osmium compounds; 2.06(3) - 2.10(3) Å [Allen et al. 1977].

The O-S bond length for the diethylsulphoxide ligand of 1.576(21) is relatively long compared with other reported bond lengths; 1.543(8) Å in the ruthenium analogue, 1.541(7) Å in the dimeric ruthenium complex $[Ru(NO)Br_3(Et_2SO)]_2$ [Fergusson et al. 1976], and 1.461(7) Å found in a osmium dimethylsulphoxide complex [Cabeza. et al. 1986]. Page (1978) surveyed the bond lengths for sulphur and oxygen coordinated organosulphoxide ligands, and there is little difference in the bond lengths for the different modes of coordination. The oxygen bound organosulphoxide bond lengths were in the range 1.48 - 1.56 Å and the sulphur bound ligands in the range 1.43 - 1.53 Å. Most of the compounds investigated contained dimethylsulphoxide.

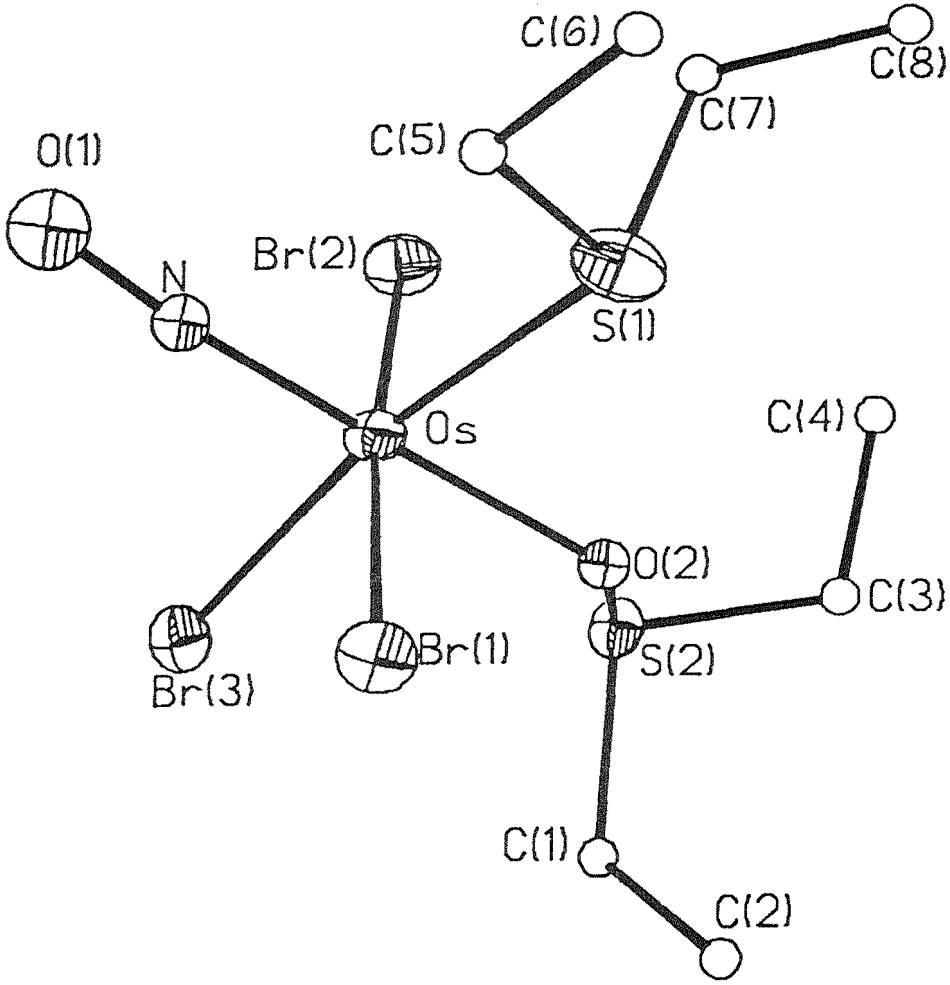


FIGURE 7.3

Perspective view of the structure of $Os(NO)Br_3(Et_2S)(Et_2SO)$

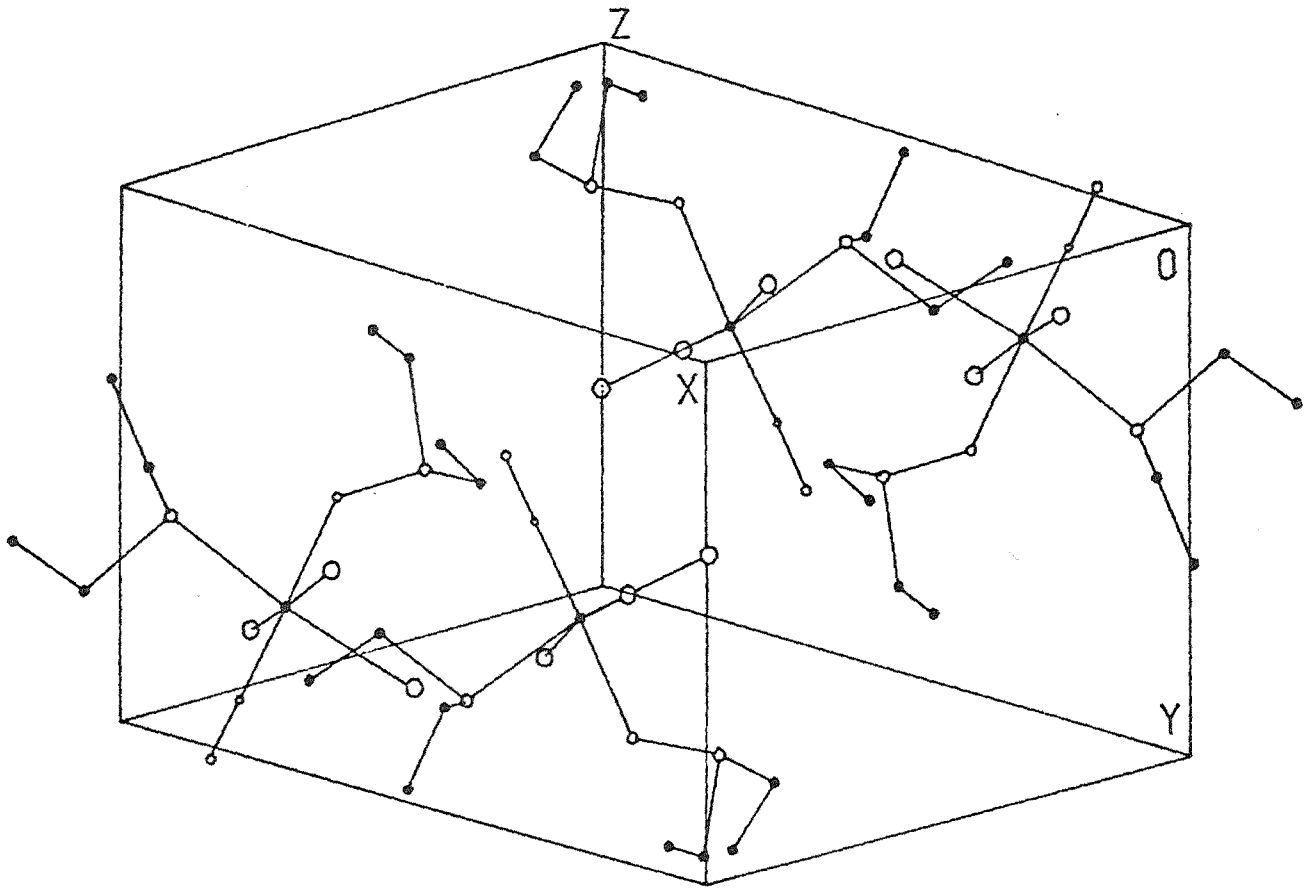


FIGURE 7.4

Unit cell packing for $Os(NO)Br_3(Et_2S)(Et_2SO)$

Atom	x	y	z	U
Os	2374(1)	1804(1)	880(1)	29(1)*
Br(1)	852(3)	1973(3)	1509(2)	44(1)*
Br(2)	3976(3)	1933(4)	371(2)	47(1)*
Br(3)	3423(3)	472(3)	2213(2)	44(1)*
S(1)	1336(8)	3452(10)	-217(6)	54(4)*
S(2)	3884(7)	4399(7)	2017(5)	33(3)*
O(1)	1835(22)	-1155(25)	49(17)	57(6)
O(2)	2771(16)	3989(18)	1443(13)	26(4)
N	1990(20)	34(23)	410(15)	29(5)
C(1)	241(37)	2103(39)	-814(29)	71(10)
C(2)	-488(33)	3001(37)	-1464(27)	67(10)
C(3)	1907(34)	3960(38)	-1036(26)	59(9)
C(4)	1592(36)	5561(40)	-1411(29)	71(10)
C(5)	3677(32)	4535(33)	3119(23)	40(7)
C(6)	2754(37)	5550(44)	3195(31)	81(12)
C(7)	3914(28)	6398(27)	1734(20)	31(8)
C(8)	4187(33)	6555(36)	881(25)	54(8)

TABLE 7.9

Atom coordinates (x 10^4) and temperature factors(x 10^3) for $Os(NO)Br_3(Et_2S)(Et_2SO)$.

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os	27(1)	34(1)	26(1)	-4(1)	6(1)	-9(1)
Br(1)	34(2)	52(2)	46(2)	0(17)	12(3)	-2(2)
Br(2)	39(2)	60(2)	44(2)	-4(2)	16(3)	-5(2)
Br(3)	44(3)	38(1)	49(2)	5(2)	12(3)	3(2)
S(1)	38(6)	78(6)	42(6)	8(5)	6(8)	0(59)
S(2)	25(5)	30(3)	37(5)	-2(3)	-2(6)	-3(3)

TABLE 7.10

Anisotropic temperature factors ($Å^2 \times 10^3$) for $Os(NO)Br_3(Et_2S)(Et_2SO)$

The infrared spectrum for Et_2SO shows a shift in the ν(SO) absorbance to 940 cm^{-1} in the complex from 1050 cm^{-1} in the free ligand and this suggests that there is some π-backbonding into the vacant antibonding orbital of the diethylsulphoxide. Osmium readily binds to sulphur [Cruz-Garritz et al. 1983; Elliott et al. 1982; Maheu et al. 1983] and sulphur coordination of organosulphoxide ligands seems to be more common [Cabeza et al. 1986]. It may be that steric factors are responsible for the oxygen coordination for the complex studied in this work. The sulphur to osmium bond length of 2.393(9) Å is quite different to many of the reported values; 2.324(2) Å [Cabeza et al. 1986], 2.507 Å [Cruz-Garritz et al. 1983], 2.474(3) Å [Elliott et al. 1982], 2.414(8) Å, 2.396(8) Å [Maheu et al. 1983], but there are no complexes that are directly comparable.

The Os-N-O bond angle of 171.4(29)°, although showing a relatively large standard deviation, clearly indicates linearly bound NO. The osmium to nitrogen bond length of 1.712(22) Å is similar to that reported by Haymore and Ibers (1975b) for linear and bent coordinated nitric oxide in another osmium complex; 1.776(7) Å for linear and 1.771(7) Å for the bent ligand, whereas Wilson and Ibers (1979) found a much longer Os-N bond length for a bent nitrosyl ligand; 1.915(6) Å. The nitrogen to oxygen bond length of 1.148(31) Å is significantly shorter than found for other osmium nitrosyl structures, but similar to that found by Page. Page found a bond length of 1.16(1) Å for the dimeric ruthenium complex $[Ru(NO)Br_3(Et_2SO)]_2$ and 1.09(1) Å for the ruthenium analogue. These values compare with Haymore and Ibers (1975b) lengths of 1.195(8) Å for a linear ligand, and 1.213(13) Å for the bent ligand. Wilson and Ibers (1979) found a length of 1.193(6) Å for a bent ligand.

The osmium to bromine bond lengths are in the range 2.502(4) - 2.518(4) Å and are similar to those found in other structures; 2.481(1) - 2.499(1) Å [Cotton et al. 1984], and 2.425(2) - 2.462(1) Å [Agaskar et al. 1986]. The shortest Os-Br bond length is not opposite the diethylsulphide but is opposite another bromine atom.

The carbon to sulphur and carbon to carbon bond lengths are similar to that found in the ruthenium analogue and the other complexes [Fergusson et al. 1976; Coll et al. 1987a]

It is likely that the original structure solution attempted in the space groups Cc and C2/c (Section 7.3.2) failed because of the incorrect space group assignment rather than the fact that it was based on Wycoff-ω scans. Although the Wycoff-ω scan technique is not used routinely, it has been used by other workers in this department with satisfactory results.

It is interesting to note that when the data collection was carried out on the basis of a centred lattice there were still systematic absences obtained that were consistent with known space groups. It seems that consistent systematic absences do not act as an indicator of the correctness of the space group assignment. This point is discussed in more detail in Chapter 11 because the same problem was encountered in several data collections in this thesis.

The standard deviations in the bond lengths and bond angles are quite high. The ratio of observations to variables is adequate at approximately ten to one and the variation is likely to be due to the heavy osmium atom dominating the scattering making the model relatively insensitive to the light atom positions.

The bond lengths are given in Table 7.11 and the bond angles in Table 7.12.

Bond	Length	Bond	Length
Os - Br(1)	2.518(4)	Os - Br(2)	2.502(4)
Os - Br(3)	2.507(3)	Os - S(1)	2.393(9)
Os - N	1.712(22)	Os - O(2)	2.074(17)
S(1) - C(1)	1.952(62)	S(1) - C(3)	1.752(49)
S(2) - O(2)	1.576(21)	S(2) - C(5)	1.816(52)
S(2) - C(7)	1.764(25)	C(1) - C(2)	1.453(54)
C(3) - C(4)	1.595(55)	C(5) - C(6)	1.440(80)
C(7) - C(8)	1.607(66)	N - O(1)	1.148(31)

TABLE 7.11

Bond lengths (Å) for $Os(NO)Br_3(Et_2S)(Et_2SO)$

Bond	Angle	Bond	Angle
Br(1) - Os - Br(2)	172.7(1)	Br(1) - Os - Br(3)	90.3(1)
Br(1) - Os - Br(3)	88.4(1)	Br(1) - Os - S(1)	84.1(3)
Br(2) - Os - S(1)	96.1(3)	Br(3) - Os - S(1)	169.4(2)
Br(1) - Os - N	94.2(10)	Br(2) - Os - N	92.9(10)
Br(3) - Os - N	91.2(8)	S(1) - Os - N	98.1(8)
Os - S(1) - C(3)	115.0(14)	Os - N - O	174.3(29)
O(2) - S(2) - C(7)	98.3(12)		

TABLE 7.12

Bond angles (deg) for $Os(NO)Br_3(Et_2S)(Et_2SO)$

7.4 THE CRYSTAL AND MOLECULAR STRUCTURE OF TRANS-[TRIBROMO(NITROSYL)BIS(DIETHYLPHENYLPHOSPHINE)-RUTHENIUM(II)] $Ru(NO)Br_3(Et_2PPh)_2$

7.4.1 Introduction

The structure of $Ru(NO)Br_3(Et_2PPh)_2$ was determined because it was not possible to distinguish between the trans and the cis facial isomers by ^1H n.m.r. spectroscopy. X-ray powder and ^1H n.m.r. spectra of the analogous chloro- and iodo- complexes are very similar to $Ru(NO)Br_3(Et_2PPh)_2$ which suggests that the three complexes exist in the same isomeric form. The structure determination described here found that the complex was the trans isomer.

7.4.2 Data Collection

A red block shaped crystal was placed on the diffractometer and centred manually. Refined cell parameters and standard deviations were obtained from the least squares refinement of 25 accurately centred reflections. A monoclinic unit cell determined from precession photography was found and the data collection was carried out on the basis of this cell. The mosaicity of several reflections was checked in different directions through the crystal and the data collection was carried out using the ω-scan technique. Crystal stability was monitored by recording three standard reflections every 100 reflections and no significant variation was observed. The intensities of 2272 reflections were measured. Of these 1791 were unique with an intensity greater than 3σ and were used in the

structure solution and refinement. Analysis of the systematic absences showed that the correct space group was $P2_1/c$.

The crystal data and experimental parameters are summarised in Tables 7.13 and 7.14.

7.4.3 Structure Solution and Refinement

The data was treated for Lorentz and polarisation effects and the position of the ruthenium atom deduced from the Patterson map. A difference map revealed the other heavy atoms and the lighter atoms were located from subsequent difference maps.

The absorption correction was based on Ψ-scans and an ellipsoidal model was used. All the heavy atoms as well as the nitrogen and the oxygen atoms were assigned anisotropic thermal parameters and the carbon atoms isotropic thermal parameters. Hydrogen atoms were constrained to ride on the carbon atoms with calculated bond lengths and angles. The hydrogen isotropic thermal vibration parameters were fixed at 1.2 times that of the adjacent carbon atoms. The standard deviations in the atom positions and in the bond lengths and angles are low and show that the final structure is well refined. A weighted least squares procedure allowing the weighting parameter to vary was used at the end of the refinement. This led to a final R of 0.0415, a weighted R of 0.0430, and a goodness of fit of 1.248.

Comparison of the observed and and calculated structure factors showed no evidence of extinction. The final electron density difference map showed no anomalies and the peaks in the difference map are concentrated around the heavy atoms and are most likely to be associated with residual anisotropy.

Formula	$Ru(NO)Br_3(Et_2PPh)_2$
Formula weight	703.20
Crystal system	monoclinic
Space group	$P2_1/c$
a	13.505(2) Å
b	7.389(0) Å
c	24.492(3) Å
$\alpha = \gamma$	90.000(0)°
β	91.22(1)°
Volume	2443.43(47) $Å^3$
F(000)	1376
μ	56.32 cm^{-1}

TABLE 7.13

Crystal data for $Ru(NO)Br_3(Et_2PPh)_2$

Temperature	263 K
Radiation	Mo K_α (0.71069a)
Bragg angle range	5 - 50^o
Scan range	1.6^o
Scan speed	fixed 5.86 $^o min^{-1}$.
Crystal dimensions	0.20mm x 0.10mm x 0.43mm
Crystal volume	0.0086 mm^3
Calculated density	1.91 g cm^{-3}
Molecules per unit cell	four
Mosaicity	0.28^o
Observed Reflections	2277
Reflections used in refinement	1791
Ratio observations to variables	1791:153(11.7:1)
Range of transmission Factors	0.624 - 0.959

TABLE 7.14

Data collection parameters for $Ru(NO)Br_3(Et_2PPh)_2$

7.4.4 Description of the Structure

The structure consists of discrete molecules in which three bromine atoms, two diethylphenylphosphine ligands, and a NO group are coordinated to the ruthenium atom in an octahedral manner. The bromine atoms are coordinated in a meridional configuration and the phosphine ligands are trans to each other. The asymmetric unit is shown in Figure 7.5 and the unit cell packing in Figure 7.6. The atom coordinates and the anisotropic temperature factors are given in Tables 7.15 and 7.16.

7.4.5 Discussion

The nitrosyl ligand is coordinated in a linear fashion as has been seen for the other structures [Haymore and Ibers 1975a; Schultz et al. 1974; Fergusson et al. 1976; Coll et al. 1987a] and the Ru-N bond lengths of 1.776(10) Å, and N-O of 1.108(13) Å are similar to reported values and indicate substantial π-interaction between the metal centre and the nitrogen.

It is interesting to note that in this structure there is some shortening of the bromine to ruthenium bond for the bromine that is opposite the nitrosyl group; 2.489(1) Å compared with 2.529(1) and 2.533(1) Å and is also shorter than that found for other ruthenium(II) complexes; 2.500(2) - 2.509(2) Å for $Ru(NO)Br_3(Et_2S)(Et_2SO)$, and 2.493(1) - 2.508(9) Å for $Ru(NO)Br_3(n\text{-}Pr_2S)_2$ [Coll et al. 1987a]. This type of effect has been noted in the structures of nitrosyl complexes with chlorine ligands and is attributed to the better σ-donating ability of the chlorine atom relative to the nitrosyl group [Fergusson & Rodley 1975; Fergusson et al. 1976].

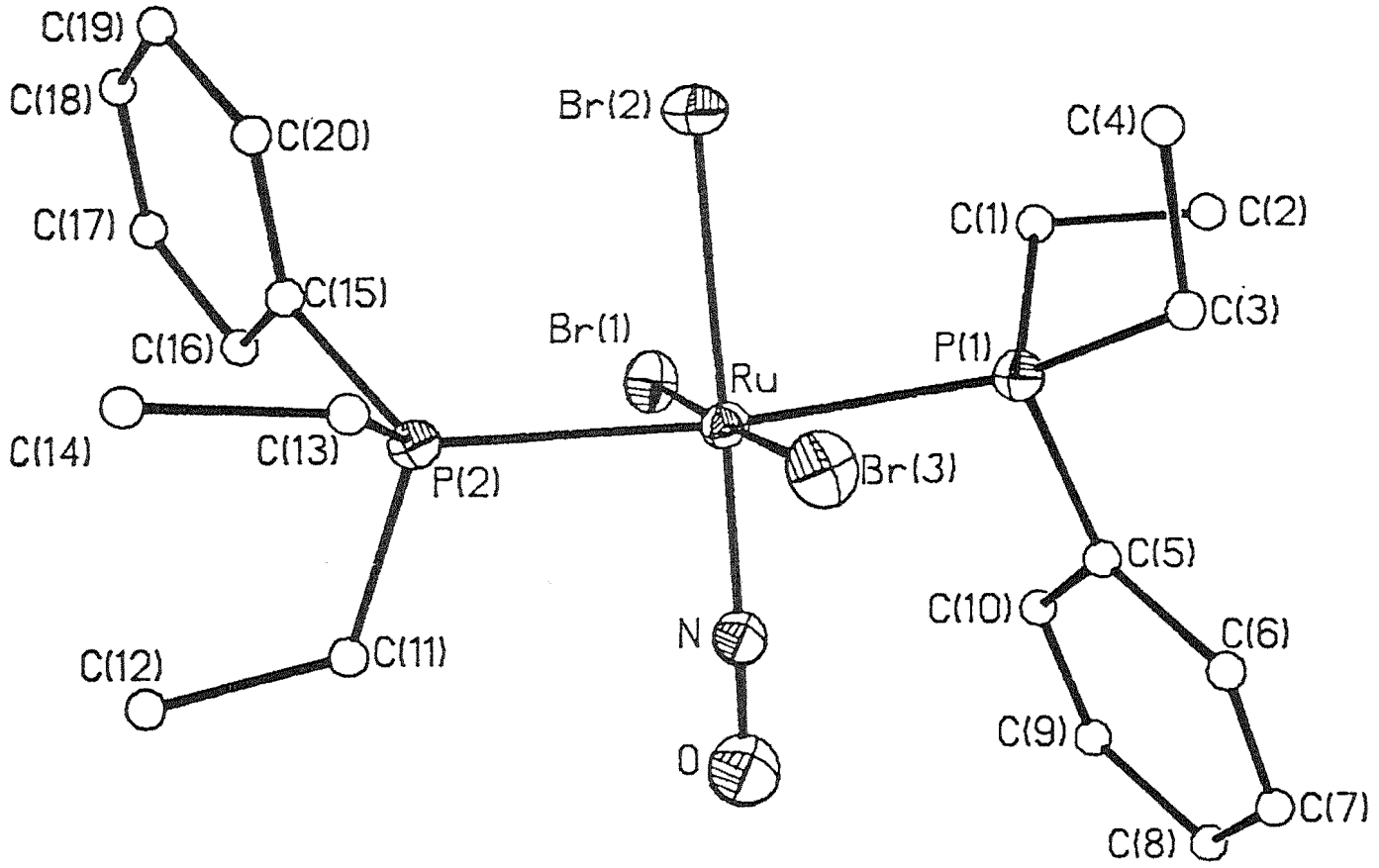


FIGURE 7.5

Perspective view of the structure of $Ru(NO)Br_3(Et_2PPh)_2$

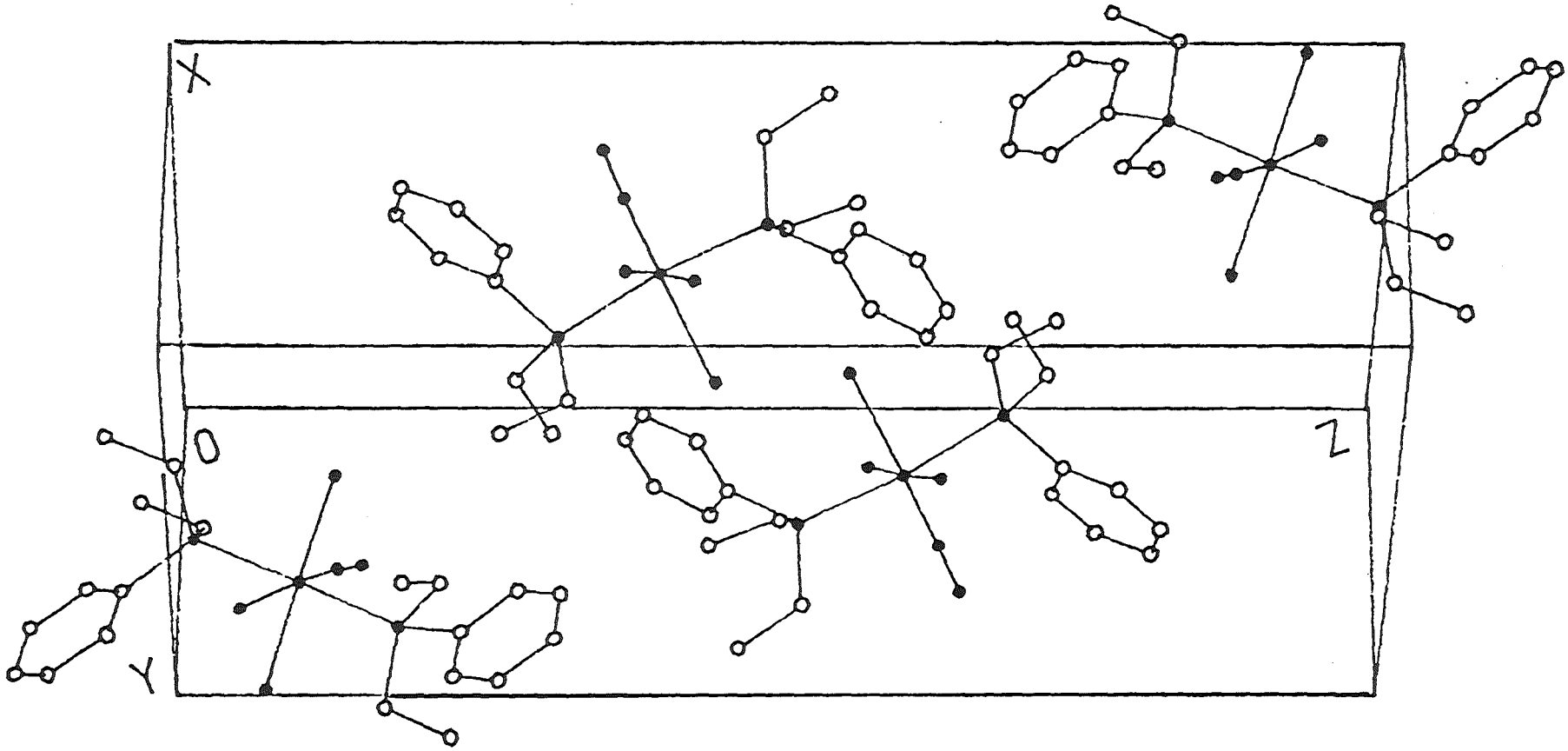


FIGURE 7.6

Unit cell packing for $Ru(NO)Br_3(Et_2PPh)_2$

Atom	x	y	z	U
Ru	2753(1)	5652(1)	6024(1)	16(1)*
Br(1)	8702(1)	6323(1)	4258(1)	24(1)*
Br(2)	3857(11	3460(1)	5563(1)	26(1)*
Br(3)	4236(1)	7535(1)	6316(1	26(1)*
P(1)	7025(2)	8879(3)	8147(1)	19(1)*
P(2)	2632(2)	7190(3)	5145(1)	19(1)*
O	1280(7)	7936(10)	6505(4)	36(3)*
N	1882(8)	7107(11)	6335(5)	19(3)*
C(1)	2704(9)	1483(14)	6778(5)	25(2)
C(2)	2800(10)	384(15)	7294(6)	35(3)
C(3)	4180(10)	3953(14)	7202(5)	28(2)
C(4)	4997(10)	3046(15)	6897(6)	31(3)
C(5)	2124(9)	4680(13)	7369(5)	24(2)
C(6)	2427(10)	5745(15)	7816(6)	33(3)
C(7)	1768(10)	6374(15)	8174(6)	31(3)
C(8)	752(11)	5983(16)	8125(6)	40(3)
C(9)	447(11)	4956(17)	7679(6)	38(3)

TABLE 7.15

Atom coordinates (x 10^4) and temperature factors (x 10^3) for $Ru(NO)Br_3(Et_2PPh)_2$.

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U
C(10)	1109(11)	4356(15)	7306(6)	33(3)
C(11)	1624(9)	8812(13)	5180(5)	23(2)
C(12)	1354(11)	9943(17)	4666(6)	39(3)
C(13)	3741(10)	8404(14)	4978(5)	28(2)
C(14)	3786(10)	9321(15)	4422(6)	34(3)
C(15)	2355(9)	5764(13)	4559(5)	22(2)
C(16)	1371(10)	5384(14)	4406(5)	27(2)
C(17)	1201(10)	4239(15)	3946(5)	30(3)
C(18)	1917(10)	3452(15)	3699(6)	30(3)
C(19)	2919(10)	3819(15)	3839(6)	33(3)
C(20)	3113(9)	4932(14)	4286(5)	27(2)

TABLE 7.15 CONTINUED

Atom coordinates (x 10^4) and temperature factors(x 10^3) for $Ru(NO)Br_3(Et_2PPh)_2$.

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru	14(1)	19(1)	15(1)	-2(1)	0(1)	1(1)
Br(1)	21(1)	29(1)	24(1)	0(1)	-4(1)	6(1)
Br(2)	25(1)	28(1)	25(1)	-4(1)	4(1)	9(1)
Br(3)	21(1)	28(1)	30(2)	1(1)	-4(1)	-5(1)
P(1)	19(2)	20(1)	18(2)	1(1)	-1(2)	0(1)
P(2)	19(2)	19(1)	19(2)	-1(1)	-1(2)	3(1)
O	26(6)	34(4)	46(7)	-3(5)	4(8)	9(4)
N	17(6)	20(5)	21(7)	2(5)	-2(8)	-6(5)

TABLE 7.16

Anisotropic temperature factors ($Å^2 \times 10^3$) for $Ru(NO)Br_3(Et_2PPh)_2$

The ruthenium to phosphorus bond lengths of 2.431(3) Å and 2.440(3) Å are typical for six coordinate ruthenium complexes containing two triphenylphosphine ligands which fall in the range 2.41 - 2.44 Å [Haymor & Ibers 1975a].

The carbon to phosphorus and carbon to carbon bonds are all similar to those reported for other complexes [Fergusson et al. 1976; Coll et al. 1987a; Haymore & Ibers 1975a; Schultz et al. 1974; Roesky et al. 1984; Goldberg et al. 1975; Mingos & Ibers 1971b]

Two similar structures to the present one have been previously reported; $Ru(NO)Cl_3(PPh_3)_2$ [Haymore & Ibers 1975a] and $Ru(NO)Cl_3(MePPh_2)_2$ [Schultz et al. 1974]. For these complexes the organophosphines are in a trans arrangement. In the structures of the similar complexes $M(NS)Cl_3(PPh_3)_2$ for M = Os, Ru the phosphines were also found to be trans [Roesky et al. 1984]. Complexes with the organophosphines in a cis arrangement are known. The dimethylphenylphosphine and dimethylphenylarsine complexes $Ru(NO)Cl_3(Me_2EPh)_2$ E = P, As, exist in the cis facial configuration [Seddon & Seddon 1984; Townsend & Coskran 1971]. In this analysis the more common trans configuration was found. In fact the cis facial arrangement is only found for the two cases mentioned [Seddon & Seddon 1984] and this may relate to the short reaction times used in their preparation, as the cis facial isomer was found to undergo isomerisation readily to the trans isomer upon heating [Townsend & Coskran 1971].

The claim of Seddon & Seddon (1984) that complexes of the form $Ru(NO)X_3L_2$ exist almost exclusively the trans isomer is supported by the structure determined in this work. The most likely explanation for this is that the bulky phenyl groups makes the isolation of an

isomer with the organophosphine ligands cis to each other unfavourable for steric reasons [Haymore & Ibers 1975a; Schultz et al. 1974; Goldberg et al. 1975]. This explanation is supported by the fact that the only known cis isomers are those with the less bulky ligands Me_2PPh and Me_2AsPh [Townsend & Coskran 1971]. The isolation of other dimethylphenylphosphine and arsine complexes, elucidation of their structures, and a study of the cis - trans isomerisation would be an interesting area for new work.

The bond lengths are given in Table 7.17 and the bond angles in Table 7.18

Bond	Length	Bond	Length
Ru - Br(1)	2.533(1)	Ru - Br(2)	2.489(1)
Ru - Br(3)	2.529(1)	Ru - P(1)	2.431(3)
Ru - P(2)	2.440(3)	Ru - N	1.776(10)
N - O	1.108(13)	P(1) - C(1)	1.817(11)
P(1) - C(3)	1.824(14)	P(1) - C(5)	1.819(14)
P(2) - C(11)	1.814(11)	P(2) - C(13)	1.796(13)
P(2) - C(15)	1.795(13	C(1) - C(2)	1.495(20)
C(3) - C(4)	1.480(20)	C(5) - C(6)	1.401(17)
C(6) - C(7)	1.345(19)	C(7) - C(8)	1.406(19)
C(9) - C(10)	1.365(21)	C(10) - C(5)	1.397(19)
C(11) - C(12)	1.521(21)	C(13) - C(14)	1.503(21)
C(15) - C(16)	1.401(17)	C(16) - C(17)	1.423(17)
C(17) - C(18)	1.290(18)	C(18) - C(19)	1.414(19)
C(19) - C(20)	1.390(18)	C(20) - C(15)	1.380(17)

TABLE 7.17

Bond lengths (Å) for $Ru(NO)Br_3(Et_2PPh)_2$

Bond	Angle	Bond	Angle
Br(2) - Ru - Br(3)	90.4(0)	Br(2) - Ru - N	175.4(3)
Br(1) - Ru - Br(3)	178.2(1)	Ru - N - O	174.1(9)
P(1) - Ru - P(2)	173.9(1)	P(1) - Ru - Br(1)	90.0(1)
Ru - P(1) - C(1)	114.9(5)	Ru - P(1) - C(3)	117.9(4)
Ru - P(1) - C(5)	109.0(4)	Ru - P(2) - C(11)	108.1(4)
Ru - P(2) - C(13)	113.5(5)	Ru - P(2) - C(15)	115.8(4)
P(1) - C(1) - C(3)	104.8(6)	C(5) - C(6) - C(7)	121.2(12)
C(7) - C(8) - C(9)	117.0(13)	C(15) - C(16) - C(17)	117.9(11)
C(18) - C(19) - C(20)	117.9(12)		

TABLE 7.18

Bond angles (deg) for $Ru(NO)Br_3(Et_2PPh)_2$

7.5 THE CRYSTAL AND MOLECULAR STRUCTURE OF DICHLORO(NITROSYL)BIS(DIETHYLPHENYLPHOSPHINE)-(2-METHOXYETHANOATE)OSMIUM(II)

$Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$

7.5.1 Introduction

During the attempted preparation of the complex $Os(NO)Cl_3(Et_2PPh)_2$ a pale orange crystalline material was isolated and found to have an absorbance in its infrared spectrum at 1090 cm^{-1}. This absorbance is in the correct region for coordinated diethylphenylphosphineoxide and it was concluded that some oxidation of the ligand had occurred during the preparation. The X-ray structure was undertaken to determine the stereochemistry of the complex. However, the X-ray analysis found that there was no diethylphenylphosphineoxide present, and that the product of the reaction was $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$ which contained a coordinated 2-methoxyethanoate ligand. The absorbance at 1090 cm^{-1} in the infrared spectrum is also in the region expected for an ether linkage.

7.5.2 Data Collection

A large block shaped pale orange coloured crystal was placed on the diffractometer and centred manually. Refined cell parameters and standard deviations were obtained from the least squares refinement of 25 accurately centred reflections. A monoclinic cell was determined and the mosaicity of several reflections was checked in different directions through the crystal. The data collection was carried out

using the ω-scan technique. Crystal stability was monitored by recording three standard reflections every 100 reflections and no significant variation was observed. The intensities of 4123 reflections were measured. Of these 2848 were unique reflections with an intensity greater than 3σ and were used in the structure solution and refinement. Inspection of the systematic absences showed that the space group was $P2_1/c$.

The crystal data and experimental parameters are summarised in Tables 7.19 and 7.20.

7.5.3 Structure Solution and Refinement

The data was treated for Lorentz and polarisation effects. The osmium atom was located from the Patterson map and a Fourier difference map revealed the other heavy atoms. The lighter atoms were located from subsequent difference maps.

The absorption correction was based on Ψ-scans and an ellipsoidal model was used. All atoms were assigned anisotropic thermal parameters. No attempt was made to locate the hydrogen atoms. The standard deviations in the atom positions and in the bond lengths and angles are low and show that the structure is well refined. A weighted least squares procedure allowing the weighting parameter to vary was used at the end of the refinement. This led to a final R of 0.0482, a weighted R of 0.0464, and a goodness of fit of 1.520.

Comparison of the observed and and calculated structure factors showed no evidence of extinction. The final electron density difference map showed no anomalies and the peaks in the difference map

Formula	$Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$
Formula weight	698.61
Crystal system	monoclinic
Space group	$P2_1/c$
a	10.869(1) Å
b	11.381(1) Å
c	22.673(2) Å
$\alpha = \gamma$	$90.00(0)^{\circ}$
β	$102.17(1)^{\circ}$
Volume	2741.5(10) $Å^3$
F(000)	1388
μ	49.93 cm^{-1}

TABLE 7.19

Crystal data for $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$

Temperature	163 K
Radiation	Mo K_α (0.71069a)
Bragg angle range	5 - 45°
Scan range	1.6°
Scan speed	fixed 9.00 $^\circ min^{-1}$.
Crystal dimensions	0.14mm x 0.14mm x 0.30mm
Crystal volume	0.006 mm^3
Calculated density	1.69 g cm^{-3}
Molecules per unit cell	four
Mosaicity	0.25°
Observed Reflections	4123
Reflections used in refinement	2848
Ratio observations to variables	2848:289(9.8:1)
Range of transmission factors	0.583 - 0.679

TABLE 7.20

Data Collection parameters for

$Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$

are concentrated around the heavy atoms and are most likely to be associated with residual anisotropy.

7.5.4 Description of the Structure

The structure consists of well separated molecules in which two chlorine atoms, two Et_2PPh ligands, an NO group and a $CH_3OCH_2CH_2O$ ligand are coordinated to the osmium in an octaherdal manner. The $CH_3OCH_2CH_2O$ ligand is coordinated opposite the NO group and the phosphine ligands are trans to each other.

The asymmetric unit is shown in Figure 7.7 and the unit cell packing in Figure 7.8. The atom coordinates and the anisotropic temperature factors are given in Tables 7.21 and 7.22.

7.5.5 Discussion

As was mentioned in Section 7.2 there is little data available on osmium structures of this type. The reported bond lengths cited in the text are mainly from organometallic structures.

The nitric oxide is coordinated in the linear mode with a Os-N-O bond angle of $177.3(8)^{o}$. The osmium to nitrogen bond length is relatively long at 1.837(10) Å compared with 1.712(22) A that was found in $Os(NO)Br_3(Et_2S)(Et_2SO)$ and lies at the top end of the range of other reported values; 1.776(7) - 1.915(6) Å [Haymore & Ibers 1975b; Wilson & Ibers 1979]. In addition the N-O bond length of 1.098(14) Å is significantly shorter than that found in other structures; 1.148(31) Å for $Os(NO)Br_3(Et_2S)(Et_2SO)$; and in the range of 1.09(1) - 1.16(1) Å for ruthenium structures with linear nitrosyl groups [Fergusson et al. 1976; Coll et al. 1987b]. The infrared

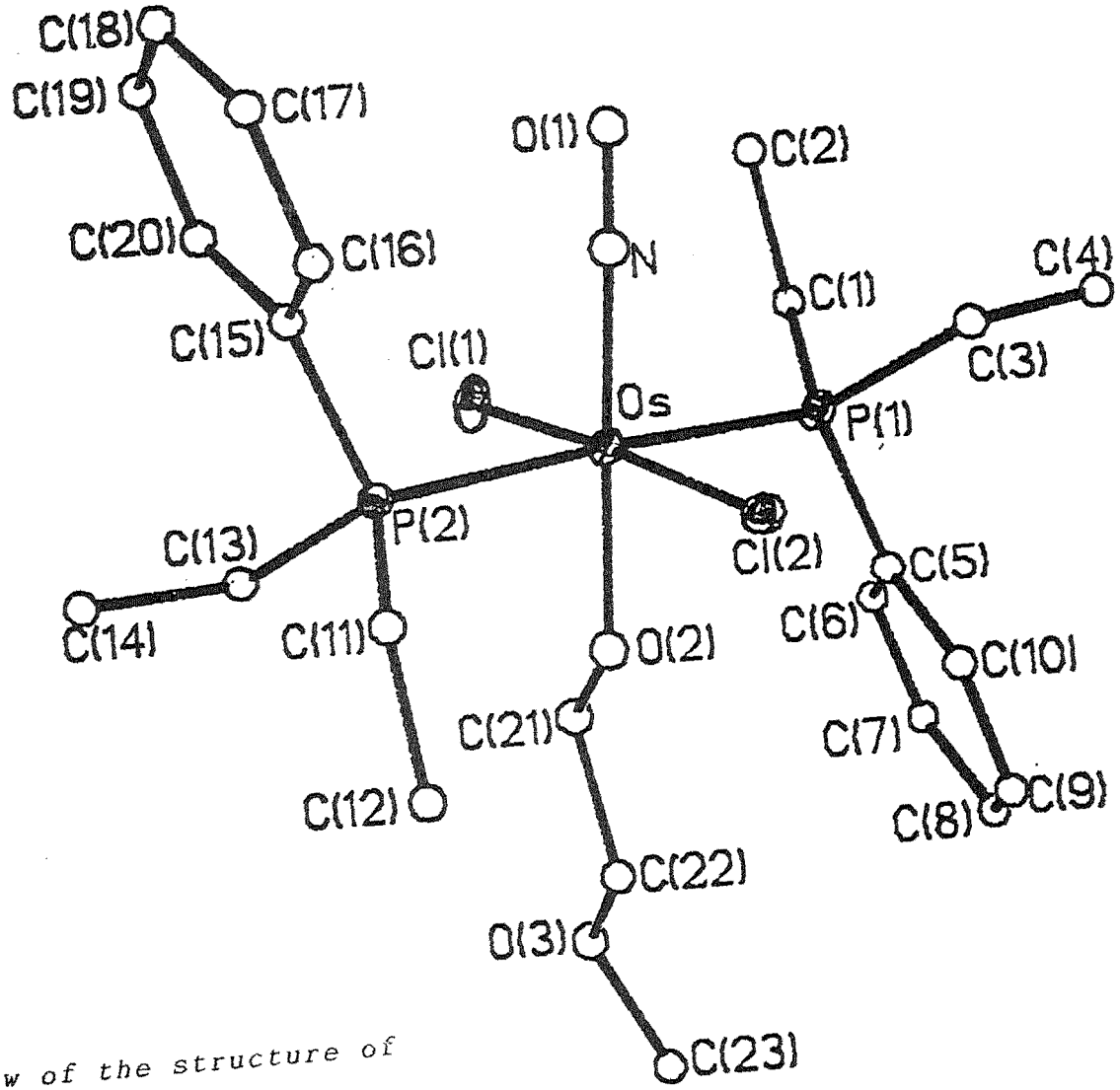


FIGURE 7.7

Perspective view of the structure of $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$

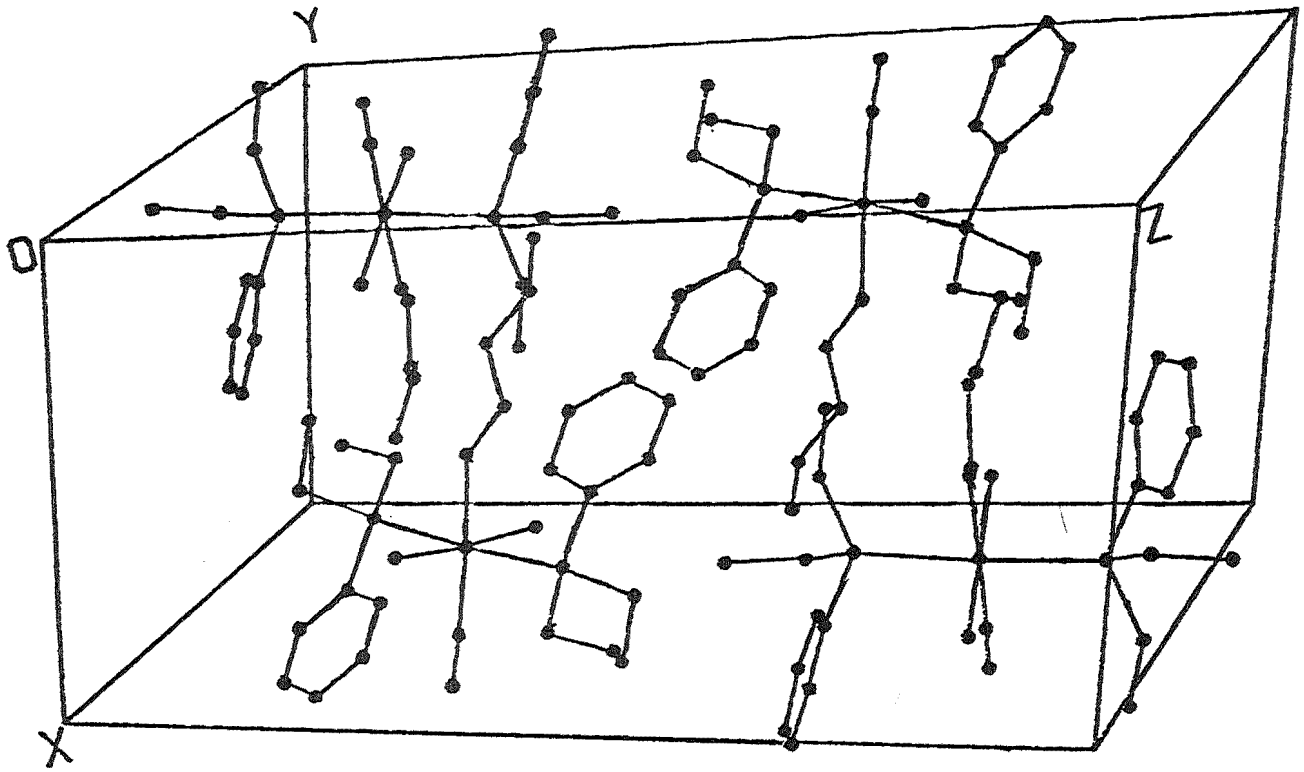


FIGURE 7.8

Unit cell packing for $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$

Atom	x	y	z	U*
Os	2507(0)	7301(0)	6466(0)	24(0)
Cl(1)	8037(3)	4699(2)	3784(1)	42(1)
Cl(2)	3221(3)	9274(2)	6698(1)	32(1)
P(1)	2294(3)	7290(3)	399(1)	30(1)
P(2)	2846(3)	8197(2)	2529(1)	23(1)
O(1)	- 95(9)	8043(10)	6424(4)	65(4)
O(2)	4287(7)	8064(7)	1547(3)	34(3)
O(3)	6956(10)	5337(8)	6289(5)	76(5)
N	870(9)	7759(8)	6425(3)	43(3)
C(1)	1229(11)	6722(11)	4884(5)	39(5)
C(2)	- 147(12)	6826(13)	4971(6)	55(5)
C(3)	1683(11)	9205(10)	5195(5)	31(4)
C(4)	1445(12)	9445(12)	4502(5)	43(5)
C(5)	3772(10)	7636(9)	5144(5)	28(4)
C(6)	4047(13)	6724(12)	4778(6)	49(5)
C(7)	5233(14)	6695(13)	4604(6)	56(6)
C(8)	6088(13)	7634(15)	4806(6)	65(6)

TABLE 7.21

Atom coordinates ($\times 10^4$) and temperature factors ($\times 10^3$) for $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$.

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U*
C(9)	5839(15)	8511(14)	5179(7)	63(7)
C(10)	4662(11)	8536(12)	5341(6)	42(5)
C(11)	3905(10)	7781(10)	8046(5)	31(4)
C(12)	5328(10)	7612(11)	7987(5)	38(4)
C(13)	3452(12)	5291(10)	7689(5)	38(5)
C(14)	3563(13)	4904(11)	8357(5)	46(5)
C(15)	1368(10)	6884(10)	7788(4)	26(4)
C(16)	1026(11)	7916(11)	8033(5)	38(5)
C(17)	- 142(11)	7974(11)	8204(5)	40(5)
C(18)	- 951(12)	7015(13)	8126(6)	48(5)
C(19)	- 610(12)	5964(13)	7871(6)	53(6)
C(20)	577(12)	5882(11)	7710(6)	42(5)
C(21)	4880(12)	6005(11)	6391(6)	101(6)
C(22)	6297(14)	6321(13)	6498(9)	78(8)
C(23)	8173(14)	5727(13)	6177(7)	66(7)

TABLE 7.21 CONTINUED

Atom coordinates (x 10^4) and temperature factors(x 10^3) for $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$.

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os	26(0)	26(0)	21(0)	0(0)	6(0)	-6(0)
Cl(1)	66(2)	29(2)	32(1)	-1(2)	10(1)	-15(2)
Cl(2)	31(2)	28(2)	36(2)	-2(1)	6(1)	-4(1)
P(1)	32(2)	37(2)	23(2)	-1(1)	9(1)	8(1)
P(2)	22(2)	28(2)	21(2)	0(0)	7(0)	0(0)
O(1)	30(6)	100(9)	64(7)	6(6)	10(5)	8(6)
O(2)	24(4)	46(5)	33(5)	-5(4)	10(4)	-14(4)
O(3)	73(8)	38(6)	130(10)	-5(6)	48(7)	3(5)
N	49(6)	56(6)	27(5)	8(4)	12(4)	-16(5)
C(1)	39(8)	59(9)	20(7)	-11(6)	3(6)	-18(7)
C(2)	37(8)	81(11)	46(8)	-6(7)	6(7)	-36(8)
C(3)	25(7)	40(7)	26(7)	12(5)	0(6)	2(6)
C(4)	42(9)	65(9)	22(7)	15(6)	0(6)	-14(7)
C(5)	27(6)	33(7)	25(6)	9(5)	10(5)	0(5)
C(6)	48(9)	59(9)	42(8)	-2(7)	14(7)	15(7)
C(7)	60(10)	76(11)	34(8)	16(8)	13(8)	22(9)
C(8)	46(9)	107(14)	43(9)	21(9)	21(9)	9(7)

TABLE 7.22

Anisotropic temperature factors ($Å^2 \times 10^3$) for $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(9)	69(12)	76(11)	49(10)	-10(8)	24(9)	-19(9)
C(10)	24(7)	67(10)	39(8)	0(7)	13(6)	-12(7)
C(11)	23(6)	51(7)	18(6)	-10(5)	2(5)	-12(6)
C(12)	20(6)	54(8)	41(7)	1(6)	4(5)	-9(6)
C(13)	50(9)	33(7)	38(8)	18(6)	25(7)	16(6)
C(14)	71(10)	51(8)	20(7)	11(6)	21(7)	9(7)
C(15)	26(7)	41(7)	13(6)	7(5)	4(5)	0(6)
C(16)	40(8)	49(8)	26(7)	9(6)	8(6)	18(6)
C(17)	27(7)	54(9)	42(8)	10(6)	12(6)	17(6)
C(18)	33(8)	80(11)	35(8)	5(7)	14(6)	19(7)
C(19)	34(9)	92(12)	35(8)	5(8)	10(7)	-15(8)
C(20)	31(8)	55(9)	43(8)	-4(6)	14(6)	-5(6)
C(21)	103(1)	112(11)	91(10)	7(8)	26(8)	9(8)
C(22)	36(9)	61(10)	144(17)	-38(11)	33(10)	17(8)
C(23)	58(10)	73(11)	78(12)	15(9)	41(9)	-18(9)

TABLE 7.22 CONTINUED

Anisotropic temperature factors ($Å^2$ x 10^3) for $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$

spectrum shows an absorbance at 1800 cm^{-1} assigned to ν(NO) which lies in the middle of the range for the reported absorbances for ν(NO). The position of this absorbance is not necessarily directly related to the bond length as is discussed in Chapter 2.

The 2-methoxyethanoate ligand is coordinated opposite the nitrosyl group. The Os-O bond length of 1.949(7) Å is significantly shorter than other Os-O values reported which lie in the range 2.06(3) - 2.10(3) Å and that for $Os(NO)Br_3(Et_2S)(Et_2SO)$ which is 2.082(17) Å. This is similar to the effect seen in nitrosyl structures containing chlorine atoms opposite the nitrosyl group [Fergusson & Rodley 1975; Coll et al. 1987b] in which the metal chlorine bond is shortened when coordinated opposite the nitrosyl group.

There is a lone pair of electrons on the oxygen atom and this means the oxygen may be bonded to a proton. If this were the case the 2-methoxyethanol ligand would be bound as a neutral ligand. As the Os-N-O system is linear this means that the NO group is bound as NO^+, and if the 2-methoxyethanol ligand is bound as the anion the osmium will be divalent. Osmium(II) would have an electron configuration spin paired d^6, and this is the more stable configuration for osmium complexes with group (V) donors [Griffith 1967]. However, if 2-methoxyethanol is bound as a neutral ligand then the osmium will be monovalent, a less characterised oxidation state [Griffith 1967].

The osmium to chlorine bond lengths of 2.390(3) and 2.398(3) Å are very similar to each other and in the middle of the range for other reported structures of; 2.290(3) - 2.345(3) Å [Agaskar et al. 1986], and 2.353(3) Å, 2.429(2) - 2.440(2) Å [Wilson & Ibers 1979].

The Os-P bond lengths of 2.427(3) and 2.428(3) Å are similar to that reported previously 2.418(2) - 2.419(2) Å [Cotton et al. 1984] and 2.424(2) - 2.459(3) Å [Wilson & Ibers 1979].

The carbon to oxygen bond lengths in the 2-methoxyethanoate ligand are similar to other reported bond lengths [Lonsdale 1962] as are the carbon to carbon bond lengths [Haymore & Ibers 1975b; Haymore & Ibers 1975a; Mingos & Ibers 1971b; Schultz et al. 1974]. The bond angles in the phenyl groups are very near the theoretical angle of 120^{o} and the bond lengths are all very consistent and are within their standard deviations of each other.

It is interesting that the 2-methoxyethanoate ligand coordinates opposite the nitrosyl group. As mentioned in Section 7.2 and 7.3 ligands that are good σ-donors and poor π-acceptors usually bind opposite the nitrosyl group. In this complex there are two such ligands the chlorine and the 2-methoxyethanol. The fact that it is the 2-methoxyethanoate that coordinates preferentially may indicate that the oxygen atom is a better σ-donor but poorer π-acceptor than chlorine. From their positions in the periodic table and using Pearsons rules this is not unexpected. This preference for oxygen being bound opposite NO has been previously reported for the complex $[NH_4][Ru(NO)Cl_4(H_2O)]Cl.H_2O$ which also has the oxygen atom of the water molecule opposite the nitrosyl when both chlorine and oxygen are present [Khodashova et al. 1972]. The bond lengths are given in Table 7.23 and the bond angles in Table 7.24.

Bond	Length	Bond	Length
Os - Cl(1)	2.390(3)	Os - Cl(2)	2.398(3)
Os - P(1)	2.427(3)	Os - P(2)	2.428(3)
Os - O(2)	1.949(7)	Os - N	1.837(10)
N - O(1)	1.098(14)	O(2) - C(21)	1.236(16)
C(21) - C(22)	1.550(18)	O(3) - C(22)	1.461(17)
O(3) - C(23)	1.467(16)	P(1) - C(1)	1.851(7)
P(1) - C(3)	1.838(6)	P(1) - C(5)	1.821(6)
P(2) - C(11)	1.836(5)		
P(2) - C(13)	1.851(5)	C(1) - C(2)	1.554(14)
C(3) - C(4)	1.562(12)	C(5) - C(6)	1.400(18)
C(6) - C(7)	1.4427(22)	C(7) - C(8)	1.427(21)
C(8) - C(9)	1.372(23)	C(9) - C(10)	1.402(22)
C(10) - C(5)	1.415(16)	C(11) - C(12)	1.592(15)
C(13) - C(14)	1.557(18)	C(15) - C(16)	1.384(17)
C(16) - C(17)	1.404(19)	C(18) - C(19)	1.411(21)
C(19) - C(20)	1.417(20)	C(20) - C(15)	1.416(17)

TABLE 7.23

Bond lengths (Å) for $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$

Bond	Angle	Bond	Angle
Cl(1) - Os - Cl(2)	175.2(1)	P(1) - Os - P(2)	175.9(1)
O(2) - Os - N	175.2(3)	Os - N - O(1)	177.3(8)
P(1) - Os - Cl(2)	89.9(1)	P(1) - Os - O(2)	91.1(2)
P(1) - C(3) - C(1)	104.1(4)	P(2) - Os - N	93.4(3)
P(1) - C(1) - C(2)	111.3(3)	P(1) - C(3) - C(4)	112.9(5)
P(1) - C(5) - C(6)	122.7(3)	C(5) - C(6) - C(7)	119.9(12)
C(8) - C(9) - C(10)	119.0(14)	P(2) - C(11) - C(12)	111.3(4)
P(2) - C(13) - C(14)	13.9(4)	P(2) - C(13) - C(11)	106.8(3)
C(15) - C(16) - C(17)	119.1(11)	C(18) - C(19) - C(20)	120.2(13)

TABLE 7.24

Selected bond angles (deg) for $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$

7.6 SUMMARY

A summary of the X-ray structural data for the platinum metal complexes studied in this section is given in Table 7.25, and the data allows for some generalisations.

The M-Br bond lengths in $Os(NO)Br_3(Et_2S)(Et_2SO)$ and $Ru(NO)Br_3(Et_2PPh)_2$ are similar, and this is expected as the metallic radii of the metals are similar (Section 8.6) and they are both in the divalent oxidation state. However, the M-Cl bond lengths for $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$ and $RhCl_3(Et_2S)_2(Et_2SO)$ are significantly different. Again this is expected as in $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$ the metal is in the divalent oxidation state, whereas in $RhCl_3(Et_2S)_2(Et_2SO)$ the metal is in the tervalent oxidation state. The shorter M-Cl bond length in $RhCl_3(Et_2S)_2(Et_2SO)$ is probably due to the higher effective charge on the tervalent rhodium.

The NO group exerts a considerable influence on the structure of the complexes studied. In all the nitrosyl complexes studied the ligand which binds opposite the NO group is a weak π-donor, either chlorine or oxygen. The trans shortening for the M-X bond when opposite the NO group reported for chloro- complexes [Fergusson & Rodley 1975] was seen for in the bromo- complex $Ru(NO)Br_3(Et_2PPh)_2$. There does not appear to be any correlation between the position of the ν(NO) stretching frequency in the infrared spectrum and the M-N or N-O bond lengths.

However, there appears to be some correlation between the position of the ν(SO) stretching frequency and the S-O bond lengths.

Bond	1	2	3	4
M-X cis.	2.339(13)-2.370(10)	2.502(4)-2.518(3)	2.529(1)-2.533(1)	2.390(3)-2.398(3)
M-X trans.			2.489(1)	
M-S	2.340(14)-2.402(11)	2.393(9)		
M-SO	2.375(9), 2.209(11)			
M-P			2.431(3)-2.440(3)	2.427(3)-2.428(3)
M-N		1.712(22)	1.776(10)	1.837(10)
M-O		2.074(17)		1.948(7)
N-O		1.148(31)	1.108(13)	1.098(14)
S-O	1.227(31), 1.700(31)	1.576(21)		
ν(SO)	1120, 940	940		
ν(NO)		1860	1860	1800

KEY

(1) $RhCl_3(Et_2S)_2(Et_2SO)$

(2) $Os(NO)Br_3(Et_2S)(Et_2SO)$

(3) $Ru(NO)Br_3(Et_2PPh)_2$

(4) $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$

TABLE 7.25

Summary of bond lengths (Å) for platinum metal complexes.

For high values of ν(SO), the S-O bond length is shorter, and the M-S bond length is longer.

In the organophosphine complexes studied here the organophosphine ligands are coordinated in the trans configuration, presumably for steric reasons.

CHAPTER 8

A REVIEW OF THE PREPARATIVE AND X-RAY STRUCTURAL CHEMISTRIES OF HALOGENO- COMPLEXES OF THE PLATINUM METALS

8.1 INTRODUCTION

In this chapter the preparative and single crystal X-ray structural chemistries of hexahalogeno- $A_n[MX_6]$ and pentahalogeno- $A_n[M(L)X_5]$ complexes of the four platinum metals Ru, Rh, Os, and Ir are reviewed. The review, which covers the years from 1967 - 1986, is limited to these topic areas in order to keep to a reasonable length.

A number of reviews have been reported which cover sections of the subject examined here. Griffith (1967) and Canterford and Colton (1968) reviewed the preparation, structural, and reaction chemistry of Ru, Rh, Os, and Ir. Babel (1967) reviewed the X-ray structural chemistry of complexes of the type $A_2[MX_6]$, and Seddon and Seddon (1984) have published a comprehensive monograph on ruthenium chemistry.

Much of the work has been reported in Russian journals, for which fortunately English translations are available. One reason for this is that the USSR is (with South Africa) the main source of the platinum metals [Skinner 1976].

Each of the four metals will be covered separately under the headings of fluoro-, chloro-, bromo- and iodo- complexes. The divisions for each halogen subheading are hexahalogeno-, pentahalogeno-, and dimetallic complexes. A summary of the structural data is given in a table at the end of each section.

8.2 RUTHENIUM

8.2.1 Fluoro- Complexes

A) Hexafluoro- Complexes

Salts of the pentavalent **hexafluororuthenate(V)** $[RuF_6]^-$ anion have been well characterised with a wide range of cations, including ClF_3^+, O_2^+, NO^+, XeF^+, XeF_5^+, $Xe_2F_3^+$ and H_3O^+ [Burns & O'Donnell 1980b; Sunder et al. 1979; Selig et al. 1978; Zemva et al. 1983; Sokolov et al. 1976; Sunder et al. 1975; Edwards et al. 1974; Sladky et al. 1969]. The anion has been produced by oxidation of the metal with F_2 and by a redox thermal dissociation of the tetravalent $A_2[RuF_6]$ salts [Zemskov et al. 1977b].

The structure of the XeF^+ salt is interesting in that the Ru atom is in an octahedral coordination with six fluorine atoms, one of which bridges to a Xe atom [Bartlett et al. 1973]. A similar situation appears to exist for the XeF_5^+ salt. The Ru-F bond lengths in the XeF^+ salt range from 1.778(16) - 1.835(13) Å for five of the bonds, and the sixth Ru-F bond that bridges to xenon is longer at 1.919(13) Å. There is also some variation in the Ru-F bond lengths for the XeF_5^+ salt, the reason for which is not obvious especially for a d^3 electronic configuration which could be expected to be associated with regular octahedral symmetry.

The tetravalent anion **hexafluororuthenate(IV)** $[RuF_6]^{2-}$ has been well characterised. It has been produced under strong oxidising conditions, and isolated with alkali metal cations and NO^+ [Sunder et al. 1979; Zemskov et al. 1977b].

B) Pentafluoro- Complexes

Photolysis of $K_2[Ru(NO)F_5]$ in a number of solvents produces the trivalent **pentafluoro(aqua)ruthenate(III)** $[Ru(H_2O)F_5]^{2-}$ anion [Komozin et al. 1983].

A divalent species **pentafluoro(nitrosyl)ruthenate(II)** $[Ru(NO)F_5]^{2-}$ was isolated as the K^+ salt by treating the analogous chloro- complex with KHF_2, and the Ba^{2+} salt was made by metathetical replacement of the K^+ salt [Sinitsyn & Svetlov 1980].

The single crystal X-ray structure of $K_2[Ru(NO)F_5]$ indicates an octahedral arrangement of the nitosyl group and fluorine atoms around the ruthenium atom [Salomov et al. 1984]. The Ru-F bond length for the F atom opposite the NO group is shorter (1.913(10) Å) than the other bonds (1.958(6) Å average).

C) Dimetallic Complexes

The KrF_2^+ salt of the monofluorobridged complex ion **μ-fluorobis[pentafluororuthenate(V)]** $[Ru_2F_{11}]^-$ originally formulated as $KrF_2 \cdot 2RuF_5$ was reinvestigated, and based on its Raman spectrum was reformulated as containing the $[Ru_2F_{11}]^-$ unit [Sokolov et al. 1976]. It appears that O_2^+ [Sunder et al. 1975] and XeF^+ salts [Sladky et al. 1969] also exist.

The **μ-oxo-bis[pentafluororuthenate(IV)]** $[Ru_2OF_{10}]^{4-}$ anion has been produced from hydrolysis of $[RuF_6]^{2-}$ [Shipachev & Zemskov 1982].

8.2.2 Chloro- Complexes

A) Hexachloro- Complexes

The **hexachlororuthenate(IV)** $[RuCl_6]^{2-}$ anion is a well characterised species, and may be isolated with a wide range of cations [Jaber et al. 1977; Cresswell et al. 1972; Campbell et al. 1985; Mit'kin et al. 1977; Kukushkin et al. 1983; Spacu & Gheorghiu 1967]. A variety of preparative methods have been used, which include either oxidation of tervalent ruthenium species with perchlorate or dichlorine, or oxidation of the metal with dichlorine at elevated temperatures.

The potassium salt has the cubic hexachloroplatinate ($K_2[PtCl_6]$) structure with a = 9.732(4) Å and Ru-Cl = 2.318(2) Å [Deloume et al. 1979].

The tervalent **hexachlororuthenate(III)** $[RuCl_6]^{3-}$ anion has not been as extensively studied as the tetravalent ion [Lee & Cho 1984; Ryabov & Zhitnikova 1969; James & McMillan 1975; Danilov et al. 1982; Prokof'eva et al. 1967; Gaylor & Senoff 1972; Drew et al. 1971]. In a number of preparative methods the compound $RuCl_3.xH_2O$ was first treated with a reducing agent to ensure that no Ru(IV) was present. The salt $K_2[RuCl_6]$ has been reported to decompose at high temperature to give the tervalent salt [Ryabov & Zhitnikova 1969]. The single crystal X-ray structure of the complex $Al(H_2O)_6[RuCl_6].4H_2O$ has been reported [Hopkins et al. 1969]. The coordination of the $[RuCl_6]^{3-}$ anion is essentially octahedral and the Ru-Cl bond lengths lie in the range 2.370(2) - 2.384(2) Å. There is some evidence for hydrogen bonding between water and the chlorine atoms. The anilinium salt

$(C_6H_5NH_3)_6[RuCl_6].3Cl$ is isostructural with the bromine analogue [Drew et al. 1971]

B) Pentachloro- Complexes

A number of monodentate ligands, neutral and charged, occur as the sixth ligand in pentachloro- ruthenium species. Some of the ligands are; N^{3-}, RCN, H_2O, CO, NO^+, $HCOO^-$, and $NH_2SO_3^-$. Most of the complexes occur with ruthenium in the tervalent oxidation state.

The diamagnetic hexavalent **pentachloro(nitrido)ruthenate(VI)** $[Ru(N)Cl_5]^{2-}$ ion isolated as the Cs^+ salt, was obtained from the reaction of sodium azide and RuO_4 in CCl_4 [Pawson & Griffith 1972; Griffith & Pawson 1973b].

It appears from their infrared spectra that the ligands RCN (R = Me, and Ph) in the tervalent **pentachloro(nitrile)ruthenate(III)** $[Ru(RCN)Cl_5]^{2-}$ species are bound to the metal through the nitrogen atom [Dehand & Rose 1979].

The **pentachloro(aqua)ruthenate(III)** $[Ru(H_2O)Cl_5]^{2-}$ ion has been well characterised and was found as one of the products of the chlorination of ruthenium metal. It has also been isolated by electrophoresis of ruthenium chloro- species and photolysis of $[Ru(NO)Cl_5]^{2-}$ or $Na_3[RuCl_6]$ [Lee & Cho 1984; Mezaraups et al. 1973; Komozin et al. 1983; Nikol'skii & Popov 1980; Cox & Wallace 1971; Fergusson & Greenaway 1978; Garif'yanov & Luchkina 1969].

The introduction of carbon monoxide as the sixth ligand to give the **pentachloro(carbonyl)ruthenate(III)** $[Ru(CO)Cl_5]^{2-}$ ion was achieved using formic acid or CO gas on various Ru(III) species. The anion has been isolated as the K^+ and Cs^+ salts [Simanova et al. 1981; Colton &

Farthing 1971; Cleare & Griffith 1969; Fergusson & Greenaway 1978]. The single crystal X-ray structure was determined on the benzyltriphenylphosphonium salt. The complex is orthorhombic with octahedral coordination around the metal. The Ru-Cl bond lengths lie in the range 2.374(6) - 2.48(3) Å and the Ru-C bond length is 1.88(5) Å [Gould et al. 1978].

The ammonium salt of **pentachloro(nitrosyl)ruthenate(III)** $[Ru(NO)Cl_5]^-$ has been reported [Pandey et al. 1982], but there is doubt over the formulation the compound, particularly the oxidation state of the metal. It is likey that the complex is the Ru(II) species described below [Coombe et al. 1983b].

The potassium salt of **pentachloro(sulphamato)ruthenate(III)** $[Ru(NH_2SO_3)Cl_5]^{3-}$ species has been reported and was produced by treatment of $K_2[RuCl_6]$ with sulphamic acid [Griffith & Pawson 1973a]. The infrared spectrum indicated that the sulphamato ligand was coordinated to the metal through the nitrogen atom.

A large number of cations (alkali metal, NH_4^+, NR_4^+, and AsR_4^+) have been used to isolate the divalent **pentachloro(nitrosyl)ruthenate(II)** $[Ru(NO)Cl_5]^{2-}$ species [Mercer & Cox 1972; Khan et al. 1983; Veal & Hodgson 1972b; Petrov et al. 1968; Sinitsyn et al. 1968; Kukushkin et al. 1983; Rubstov et al. 1969; Sinitsyn et al. 1982b]. The nitrosyl was introduced by treating Ru(III) species with either NO or NOCl. Metathetical replacement has been used to obtain one salt from another. The tetravalent salt of this anion has been reported [Sinitsyn et al. 1967; Psalides et al. 1973]. Alkali metal salts were reported to be isostructural with $K_2[Ru(NO)Cl_5]$, and it seems more likely that the divalent salt was in fact obtained.

Single crystal X-ray structures have been reported for the isostructural K^+ and NH_4^+ salts [Veal & Hodgson 1972a; Veal & Hodgson 1972b]. The NH_4^+ salt was originally reported to be isostructural with the complex $[Ru(NH_3)_5Cl]Cl_2$ [Trehoux et al. 1969] but it appears that this is in error. The Ru-Cl bond lengths for the Cl atoms trans to the NO group (2.359(2) Å K^+ and 2.357(1) Å NH_4^+) are shorter than the other Ru-Cl bond lengths (2.363(7) - 2.377(2) Å K^+ and 2.373(1) - 2.378(1) Å NH_4^+).

C) Dimetallic Complexes

Evidence for the dimeric species **tri-μ-chlorobis[trichlororuthenate(III)]** $[Ru_2Cl_9]^{3-}$ anion was obtained when the alkali metal salts $A_2[Ru(H_2O)Cl_5]$ were thermally decomposed [Fergusson & Greenaway 1978]. Magnetic studies were consistent with a Ru-Ru bond, and the single crystal X-ray structure of $Cs_3[Ru_2Cl_9]$ has confirmed this with a Ru-Ru bond length of 2.725(3) Å [Darriet 1981]. The complex anion contains three bridging chlorine atoms i.e. the two "$RuCl_6$" octahedra share a face. The Ru-Cl bond lengths for the bridging chlorine atoms are slightly longer (2.391(4) Å) than for the terminal chlorine atoms (2.332(4) Å).

The potassium salt of the **di-μ-chlorobis[tetrachlororuthenate(III)]** $[Ru_2Cl_{10}]^{4-}$ anion has also been reported from the thermal decomposition of $K_2[Ru(H_2O)Cl_5]$ [Sinitsyn et al. 1982c].

A number of complexes of ruthenium have been isolated where the sixth ligand (L) of $[Ru(L)Cl_5]^{n-}$ bridges between two ruthenium atoms. The complex anions $[Ru_2OCl_{10}]^{4-}$, $[Ru_2Cl_9H_2O]^{3-}$, $[Ru_2NOCl_9NO]^{3-}$, $[Ru_2NCl_8(H_2O)_2]^{3-}$ have been reported [Alimarin et al. 1973; Broomhead et

al. 1968; Shipachev & Zemskov 1982; Jaber et al. 1977; Deloume et al. 1981; Mukaida 1970]. The ruthenium metal atoms are in the tetravalent oxidation state, except for the nitrosyl complex where they are tervalent.

The single crystal X-ray structures of $K_4[Ru_2OCl_{10}]$ [Deloume et al. 1979] and $K_3[Ru_2NCl_8(H_2O)_2]$[Good et al. 1984] have been determined. For the oxo- complex Ru-O = 1.801(2) Å, $Ru-Cl_{ax}$ = 2.317(7) Å and $Ru-Cl_{eq}$ = 2.362(2) Å; whereas for the nitrido complex the Ru-Cl bonds are shorter at 2.353(10), and 2.369(9) Å. The Ru-N bonds are also relatively short at 1.728(9) Å indicating some multiple bond character.

8.2.3 Bromo- Complexes

A) Hexabromo- Complexes

Alkali metal salts of the **hexabromoruthenate(IV)** $[RuBr_6]^{2-}$ anion have been reported, and were formed by treatment of a variety of Ru(III) and Ru(IV) species with HBr [Fergusson & Greenaway 1978].

The tervalent complex anion **hexabromoruthenate(III)** $[RuBr_6]^{3-}$ has been isolated using large cations such as $[N(CH_2CH_2NH_3)_3]^{3+}$ and anilinium [Gaylor & Senoff 1972; Parashad et al. 1981; Drew et al. 1971]. The structure of the anilinium salt has been determined and the bromine atoms are octahedrally arranged around the ruthenium atom [Drew et al. 1971]. There are three independant Ru-Br bonds all with the same length of 2.514(5) Å.

B) Pentabromo- Complexes

The hexavalent caesium salt of **pentabromo(nitrido)ruthenate(VI)** $[Ru(N)Br_5]^{2-}$ was obtained from RuO_4 when treated with sodium azide [Pawson & Griffith 1972; Griffith & Pawson 1973b]. The infrared spectrum has been assigned with reference to the similar osmium complex $K_2[Os(N)Br_5]$ [Collin et al. 1973].

The tervalent **pentabromo(aqua)ruthenate(III)** $[Ru(H_2O)Br_5]^{2-}$ ion produced by the photolysis of the $[Ru(NO)Br_5]^{2-}$ was isolated as the K^+ salt [Nikol'skii & Popov 1980; Komozin et al. 1983].

Use of CO or formic acid on $RuBr_3 \cdot xH_2O$ or $RuCl_3 \cdot xH_2O$/HBr produced the **pentabromo(carbonyl)ruthenate(III)** $[Ru(CO)Br_5]^{2-}$ species as the Cs salt [Colton & Farthing 1971; Cleare & Griffith 1970].

The alkali metal salts of **pentabromo(nitrosyl)ruthenate(II)** $[Ru(NO)Br_5]^{2-}$ have been isolated from reaction of NOBr on $RuCl_3 \cdot xH_2O$, or by metathetical replacement of one cation for another. Organoammonium salts have also been isolated [Sinitsyn et al. 1968; Rubstov et al. 1969; Khan et al. 1983].

C) Dimetallic Complexes

The dimetallic complex ion **tri-μ-bromobis[tribromoruthenate(III)]** $[Ru_2Br_9]^{3-}$ has been isolated as alkali metal and amine salts [Fergusson & Greenaway 1978]. The proposed existence of a Ru-Ru bond was established from the single crystal X-ray structure of the 1-methyl-3-ethylimidozalium salt [Appleby et al. 1986]. The ruthenium atoms are octahedrally coordinated, and the anion consists of a confacial bioctahedron. The Ru-Ru bond length was found to be 2.87 Å, the terminal Ru-Br bond length 2.505(14) Å, and the bridging Ru-Br

bond length 2.512(11) Å. The anion (as the NBu_4^+ and $PCH_2PhPh_3^+$ salts) undergoes reversible oxidation and reduction reactions where the oxidation state of the ruthenium atoms across the Br_3 bridge can vary from Ru(II) to Ru(IV) i.e. $[Br_3Ru^{n+}Br_3Ru^{m+}Br_3]^{x-}$ where m = n = 2, 3, 4 [Coombe et al. 1983a]. Some compounds have mixed oxidation states. Salts have been isolated for the anions $[Br_3Ru^{3+}Br_3Ru^{4+}Br_3]^{2-}$ and $[Br_3Ru^{4+}Br_3Ru^{4+}Br_3]^{-}$.

The dimetallic complex **μ-oxo-bis[pentabromoruthenate(IV)]** $[Ru_2OBr_{10}]^{4-}$ has been reported and isolated with a range of cations [San Filippo et al. 1976; Griffith 1969; San Filippo et al. 1977; Hanuza et al. 1972; Mattes et al. 1975; Jezowska-Trzebiatowska et al. 1970]. However, recently it has been suggested that the complexes may be impure $A_3[Ru_2Br_9]$ [Appleby et al. 1986].

8.2.4 Iodo- Complexes

There were no reports of hexaiodo- ruthenium complexes. Two pentaiodo- complex anions have been reported **pentaiodo(aqua)ruthenate(III)** $[Ru(H_2O)I_5]^{2-}$ and **pentaiodo(nitrosyl)ruthenate(II)** $[Ru(NO)I_5]^{2-}$. Isolation of the NO complex was achieved with a number of cations using methods similar to those used for the analogous bromo- complexes [Nikol'skii & Popov 1980; Komozin et al. 1983; Khan et al. 1983; Rubstov et al. 1969; Sinitsyn et al. 1968].

Complex	Ru-X	Ru-L	Ru-Ru	Ref.
$(XeF)[RuF_6]$	1.778(16)-1.835(13), 1.919(13) bridg.			1
$(XeF_5)[RuF_6]$	1.820(12)-1.876(11)			1
$K_2[Ru(NO)F_5].H_2O$	1.958(6)* cis, 1.913(10) trans	1.72(6)		2
$K_2[RuCl_6]$	2.318(2)			3
$Al(H_2O)_6[RuCl_6].4H_2O$	2.370(2)-2.384(2)			4
$(BTP)_2[Ru(CO)Cl_5].2CH_2Cl_2$	2.374(6)-2.48(3)	1.88(5)		5
$K_2[Ru(NO)Cl_5]$	2.363(7)-2.377(2) cis, 2.359(2) trans	1.747(6)		6
$(NH_4)_2[Ru(NO)Cl_5]$	2.373(1)-2.378(1) cis, 2.357(1) trans	1.738(2)		7
$Cs_3[Ru_2Cl_9]$	2.332(4), 2.391(4) bridg.		2.725(3)	8
$K_4[Ru_2OCl_{10}]$	2.317(7) ax., 2.362(2) eq.	1.801(2)		3
$K_3[Ru_2(N)Cl_8(H_2O)]$	2.353(10), 2.369(9)	1.728(9) N		9
$(AnH)_3[RuBr_6].3(AnBr)$	2.514(5)			10
$(MeEtim)_3[Ru_2Br_9]$	2.505(14), 2.512(11) bridg.		2.87	11

References

[1] Bartlett et al. 1973 [2] Salomov et al. 1984 [3] Deloume et al. 1979 [4] Hopkins et al. 1969 [5] Gould et al. 1978 [6] Veal & Hodgson 1972a [7] Veal & Hodgson 1972b [8] Darriet 1981 [9] Good et al. 1984 [10] Drew et al. 1971 [11] Appleby et al. 1986

TABLE 8.1

Summary of structural data for ruthenium halogeno- complexes. Bond lengths in Å.

KEY

BTP = benzyltriphenylphosphonium
* = average Ru-F bond length
An = aniline

8.3 OSMIUM

The halogeno- chemistry of osmium follows closely that of ruthenium, and similar complexes have been isolated. Osmium is one of the more expensive platinum metals, however a reasonable amount of work has been carried out on it.

8.3.1 Fluoro- Complexes

A) Hexafluoro- Complexes

A number of salts of **hexafluoroosmate(V)** $[OsF_6]^-$ have been prepared, and like the ruthenium system, with unusual cations such as NO^+, AsF_2^+, XeF^+, $Xe_2F_3^+$, C_8^+ and Br_2^+ [Sunder et al. 1979; Burns & O'Donnell 1980a; Chirkst 1981; Sladky et al. 1969; Bartlett et al. 1978a; Bartlett et al. 1980; Bartlett et al. 1978b; Padma & Peacock 1981; Paine & Quarterman 1976; Frlec et al. 1967]. The salts are usually produced by the reaction of OsF_6, a powerful oxidising agent, with materials that are oxidised to form the cations for example:

$$OsF_6 + NO \rightarrow NO^+OsF_6^-$$

$$OsF_6 + C_8 \rightarrow C_8^+OsF_6^-$$

$$OsF_6 + AsF_3 \rightarrow AsF_3^+OsF_6^-$$

$$OsF_6 + Br_2 \rightarrow Br_2^+OsF_6^-$$

The graphite salt $C_8[OsF_6]$, contains OsF_6^- intercalated into graphite and is similar to other intercalated compounds of graphite [Bartlett et al. 1978a; Bartlett et al. 1978b; Bartlett et al. 1980].

The potassium salt of **hexafluoroosmate(IV) $[OsF_6]^{2-}$** was isolated from the reaction of KHF_2 with $K_2[OsX_6]$ (X = Cl, Br, and I) [Preetz & Petros 1971]. A hydrazinium salt $(N_2H_6)[OsF_6]$ has also been isolated [Frlec et al. 1967].

B) Pentafluoro- Complexes

One pentafluoro- osmate complex anion **pentafluoro(nitrosyl)osmate(II) $[Os(NO)F_5]^{2-}$** has been isolated with alkali metal cations [Sinitsyn et al. 1985a; Sinitsyn et al. 1983]. Preparation was achieved by fluorinating (using HF or KHF_2) the chloro- complex ion $[Os(NO)Cl_5]^{2-}$ or $K[OsO_3N]$.

The single crystal X-ray structure of the mixed cation salt $NaK[Os(NO)F_5].H_2O$ has been determined and contains octahedrally coordinated osmium [Salomov et al. 1984]. The bond lengths are: $Os-F_{ax}$ = 1.966(5) Å (trans to NO), $Os-F_{eq}$ (average) = 1.991(8) Å, and Os-N = 1.707(9) Å. The bond lengths in the isostructrual Cs^+ salt are similar. The Os-F bond trans to the NO group is also shortened in length.

C) Dimetallic Complexes

Hydrolysis of $K_2[OsF_6]$ produced the **μ-oxo-bis[pentafluoroosmate(IV)] $[Os_2OF_{10}]^{4-}$** anion which was isolated as the potassium salt $K_4[Os_2OF_{10}]$ [Shipachev & Zemskov 1982].

It appears that the XeF^+ salt of **μ-fluorobis[pentafluoroosmate(V)]** $[Os_2F_{11}]^-$ also exists [Sladky et al. 1969].

8.3.2 Chloro- Complexes

A) Hexachloro- Complexes

The pentavalent anion **hexachloroosmate(V)** $[OsCl_6]^-$ has been isolated with a number of cations including NR_4^+, $AsPh_4^+$, SCl_3^+. The salts are normally produced by oxidation of lower oxidation state osmium complexes (e.g. $[OsCl_6]^{2-}$) using for example Cl_2 [Dehnicke & Loessberg 1980; Magnuson 1984; Preetz & Bruns 1983; Krebs et al. 1984]. The SCl_3^+ cation was produced from the reaction of OsO_4 and SCl_2 in the presence of Cl_2 [Dehnicke et al. 1984]. The single crystal X-ray structures of the NEt_4^+ and the PPh_4^+ salts have been determined [Krebs et al. 1984; Kim et al. 1984]. The halogen coordination around the osmium is octahedral, and the Os-Cl bond lengths lie in the range 2.252(4) - 2.308(3) Å for both compounds. The Os-Cl bond lengths are short compared with those for the tetravalent $[OsCl_6]^{2-}$ ion.

Salts of **hexachloroosmate(IV)** $[OsCl_6]^{2-}$ have been isolated with a range of cations. Preparation has been achieved by reduction of $[OsCl_6]^-$, oxidation of osmium metal, or exchange of cations [Alves et al. 1982; Dehnicke & Loessberg 1980; Preetz & Bruns 1983; Fokina et al. 1981; Volkov et al. 1980]. A number of large and complex cations such as alkylammonium cations have also been used to isolate the anion from solution [Craciunescu et al. 1975b; Doadrio et al. 1978;

Craciunescu et al. 1975a; Doadrio et al. 1977; Gheorghiu 1968; Sinitsyn et al. 1985b; Bark & Brandon 1967; Moers & Langhout 1972; Bol'shakov et al. 1974]. Simple alkali metal and NH_4^+ salts have the cubic hexachloroplatinate structure [Parlog et al. 1974; Brown et al. 1967]. Three independant Os-Cl bonds were found in the X-ray structure of the PPh_4^+ salt and the Os-Cl bond lengths lie in the range 2.325(3) - 2.338(3) Å [Kim et al. 1984].

Unlike ruthenium, osmium(III) hexachloro- complexes are not well established because of the ease of oxidation of Os(III) to Os(IV). Electrolytic reduction of $H_2[OsCl_6]$ produced, on the addition of CsCl, the caesium salt of **hexachloroosmate(III)** $[OsCl_6]^{3-}$ [Emerson & Fergusson 1983]. A $Co(en)_3^{3+}$ salt has also been produced where presumably the large trivalent cation is favourable for isolating the trivalent anion [Campbell et al. 1985].

B) Pentachloro- Complexes

A greater range of complex ions of the type $A_n[Os(L)Cl_5]$ have been reported for osmium compared with ruthenium, where L = N^{3-}, NS^+, RCN, H_2O, PPh_3, Pyr, NCS^-, SCN^-, CO, NO^+ and NH_2SO_3. The metal oxidation state ranges from di- to hexavalent.

The hexavalent complex ion **penatchloro(nitrido)osmate(VI)** $[Os(N)Cl_5]^{2-}$ was isolated as a Cs^+ salt after treatment of potassium osmate $K_2[Os(O)_2(OH)_2]$ with sodium azide [Griffith & Pawson 1973b]. The single crystal X-ray structure of the K^+ salt has been determined three times. The first analysis [Atovmyan & Bokki 1960] appears to be incorrect whereas the last two are in essential agreement [Bright & Ibers 1969; Atovmyan & Trachev 1968]. The Os-N bond length is short

at 1.614(13) Å indicative of some multiple bonding. The Os-Cl cis bond lengths were in the range 2.359(4) - 2.367(4) Å. The long Os-Cl trans to the N^{3-} ligand of 2.605(4) Å bond is said to arise from steric effects.

A pentavalent complex $PPh_4[Os(L)Cl_5]$ for L = $NC(CCl_3)NCl(CCl_3)$ (formed from trichloroacetonitrile) has a distorted octahedral stereochemistry around the osmium, probably as a result of the large sixth ligand which is bound through nitrogen [Weber et al. 1982]. The Os-N bond length is quite short at 1.97(1) Å, as is the Os-Cl trans to the ligand of 2.279(3) Å, whereas the other Os-Cl bond lengths lie in the range 2.310(2) - 2.348(2) Å.

The thionitrosyl ligand NS coordinates to osmium in **$[Os(NS)Cl_5]^-$** and the anion was isolated with the cation $AsPh_4^+$ [Weber & Dehnicke 1984]. On the basis of the position of the NS stretch in the infrared spectrum (1340 cm^{-1}), the oxidation state of osmium was postulated as pentavalent, i.e. NS binding as NS^-. However, the result may equally well fit the ligand coordinating as NS^+ and with tervalent osmium. The latter suggestion appears more reasonable.

A number of neutral ligands (CH_3CN, H_2O, CO, PPh_3 and pyridine) form complex ions with tetravalent osmium of the form $A[Os(L)Cl_5]$ [Hasenpusch & Preetz 1977a; Muller et al. 1980; Bremard & Mouchel 1982; Bruns & Preetz 1986; Pawson & Griffith 1975; Preetz & Fichtner 1978].

Chlorination of the tervalent osmium carbonyl complexes trans $[Os(CO)X_4]$ (X = Br, I) produced **pentachloro(carbonyl)osmate(IV)** **$[Os(CO)Cl_5]^-$** which was isolated as the NEt_4^+ salt [Bruns & Preetz 1986]. The compound is easily reduced to Os(III) with Br^- and I^- ions.

Acid hydrolysis of $[OsCl_6]^{2-}$ gave the **pentachloro(aqua)osmate(IV)** $\mathbf{[Os(H_2O)Cl_5]^-}$ ion which was isolated as the K^+ salt [Muller et al. 1980; Hasenpusch & Preetz 1977a].

Potassium, caesium and tetrabutylammonium salts of **pentachloro(acetonitrile)osmate(IV)** $\mathbf{[Os(CH_3CN)Cl_5]^-}$ were obtained from the irradiation of $[OsCl_6]^{2-}$ or $[OsCl_5I]^{2-}$ in acetonitrile [Hasenpusch & Preetz 1977a]

Both the NCS^- SCN^- complexes $\mathbf{[Os(NCS)Cl_5]^{2-}}$ and $\mathbf{[Os(SCN)Cl_5]^{2-}}$ were formed when $[OsCl_5I]^{2-}$ was treated with $(SCN)_2$ [Preetz & Horns 1984]. The salts were isolated with the NBu_4^+ cation.

The tervalent complex ions $[Os(L)Cl_5]^{2-}$ containing the ligands L = H_2O, CO, NO^+ and NH_2SO_3 have been reported. The photolysis of $[Os(NO)Cl_5]^{2-}$ was used to produce the **pentachloro(aqua)osmate(III)** $\mathbf{[Os(H_2O)Cl_5]^{2-}}$ ion [Nikiol'skii & Popov 1980]. The treatment of $[OsCl_6]^{2-}$ with formic acid gave the **penatchloro(carbonyl)osmate(III)** $\mathbf{[Os(CO)Cl_5]^{2-}}$ ion and reduction of the tetravalent compound described above also gave the tervalent complex [Cleare & Griffith 1970; Cleare 1967; Bruns & Preetz 1986]. Alkali metal salts were prepared by metathetical replacement from $K_2[Os(CO)Br_5]$ [Johannsen & Preetz 1977]. The divalent anion has been reported as being formed [Cleare 1967; Cleare & Griffith 1967; Cleare & Griffith 1969], but was later discovered to be the tervalent anion [Cleare & Griffith 1970]. The tervalent **pentachloro(nitrosyl)osmate(III)** $\mathbf{[Os(NO)Cl_5]^-}$ ion was produced from $OsCl_5$ and NO and isolated as NO^+ and $PMePh_3^+$ salts [Weber & Dehnicke 1984]. The potassium salt of **pentachloro(sulphamato)osmate(III)** $\mathbf{[Os(NH_2SO_3)Cl_5]^{3-}}$ was obtained in a similar manner as the ruthenium analogue [Griffith & Pawson 1973a].

The divalent **pentachloro(nitrosyl)osmate(II)** $[Os(NO)Cl_5]^{2-}$ and **pentachloro(thionitrosyl)osmate(II)** $[Os(NS)Cl_5]^{2-}$ [Pandey et al. 1984] complexes can be produced where the ligands are bound as NX^+. The NO complex has been isolated with a variety of cations [Sinitsyn et al. 1975; Bol'shakov et al. 1972; Bol'shakov et al. 1973; Bol'shakov et al. 1976; Dehnicke & Loessberg 1981; Cleare & Griffith 1969].

C) Dimetallic Complexes

The **bis[tetrachloroosmate(III)]** $[Os_2Cl_8]^{2-}$ species has been isolated with $AsPh_4^+$, NR_4^+ and bis(triphenylphosphine)iminium (PPN) cations. The X-ray structure of the PPN salt indicates the structure is typical of the $[M_2Cl_8]^{n-}$ species of Re, Tc, Mo and W [Fanwick et al. 1985]. There are four chlorine atoms arranged in an approximate plannar manner around each osmium atom. The "$OsCl_4$" groups are linked through the osmium atoms, and are in a near ecllipsed arrangement. The Os-Os bond length is short (2.195(2) Å) indicative of multiple bonding. The bonding can be explained in terms of a triple bond i.e. $\sigma^2\pi^4\delta^2\delta^{*2}$. With this bonding there is no electronic barrier to rotation, and a large standard deviation was observed in the mean twist angle (4.5°). This suggests that there is no preferred configuration, and the ecllipised configuration of the chlorine atoms probably arises as a result of crystal packing.

The isolation of the **di-μ-chlorobis[pentachloroosmate(IV)]** $[Os_2Cl_{10}]^{2-}$ ion has been achieved with Cs^+ and NR_4^+ cations from the $[Os(CO)Cl_5]^-$ species [Krebs et al. 1984]. The X-ray structure has been determined for the NBu_4^+ salt and the "$OsCl_6$" octahedra share an edge [Krebs et al. 1984]. The Os-Cl terminal bond lengths lie in the

range 2.296(2) - 2.308(2) Å and the two bridging Os - Cl bond lengths are longer at 2.412(2) Å. An Os-Os distance of 3.626(1) A suggests no interaction.

The oxo- bridged species **μ-oxo-bis[pentachloroosmate(IV)]** $[Os_2OCl_{10}]^{4-}$ was produced from the hydrolysis of $[OsCl_6]^{2-}$ [Muller et al. 1980]. The Cs^+ salt has had its single crystal X-ray structure determined, and the coordination around each osmium atom is octahedral with a short Os-O bond length of 1.7777(15) Å [Tebbe & von Schnering 1973]. The Os-Cl bond length trans to the oxygen atom was found to be longer, at 2.433(7) Å, compared with a range of 2.367(6) - 2.375(6) Å for the remaining bonds.

8.3.3 Bromo- Complexes

A) Hexabromo- Complexes

It is interesting that the pentavalent complex ion **hexabromoosmate(V)** $[OsBr_6]^-$ has been reported, but only in solution [Magnuson 1984]. It is surprising that such a high oxidation state can exist for osmium in the presence of bromine.

The **hexabomoosmate(IV)** $[OsBr_6]^{2-}$ ion is a well characterised species, and has been isolated with a number of cations [Goeden & Haymore 1983; Brendel et al. 1985; Gheorghiu & Marinescu 1969; Allen et al. 1969; Bol'shalov et al. 1974; Gheorghui 1968]. The alkali metal and ammonium salts have a cubic unit cell and most of these have the $K_2[PtCl_6]$ structure [Brown et al. 1967; Parlog et al. 1974].

The **hexabromoosmate(III)** $[OsBr_6]^{3-}$ ion is much less well defined and it has been produced by electrolytic reduction of $H_2[OrBr_6]$ and

then isolated as the Cs^+ salt [Emerson & Fergusson 1983]. The large cation $[Co(en)]^{3+}$ has also been used to isolate the complex anion after $Na_2[OsBr_6]$ had been reduced with silver metal [Campbell et al. 1985].

B) Pentabromo- Complexes

The pentabromo- osmium complex ions of the form $[Os(L)Br_5]^{n-}$ where L = N (n=2), L = RCN, H_2O, Pyr, NCS^-, SCN^- (n=1) and H_2O, CO, NO^+ (n=2) have been produced and are similar to their analogous pentachloro- complexes. The formation of the hexavalent complex ion **pentabromo(nitrido)osmate(VI) $[Os(N)Br_5]^{2-}$** is unexpected and reflects the ability of the nitrido ligand to stabilise high oxidation states even in the presence of bromine [Griffith & Pawson 1973b]. The other complexes occur in the tetra- to divalent oxidation states of osmium and were prepared in much the same way as the analogous chloro- complexes. [Magnuson 1984; Hasenpusch & Preetz 1977a; Preetz & Fitchner 1978; Horns & Preetz 1986; Cleare & Griffith 1969; Johannsen & Preetz 1977; Bol'shakov et al. 1972; Sinitsyn et al. 1975; Bol'shalov et al. 1976; Nikol'skii & Popov 1980; Cleare & Griffith 1970].

C) Dimetallic Complexes

The complex $Cs_3[OsBr_6]$ spontaneously decomposes to give the caesium salt of **tri-μ-bromobis[tribromoosmate(III)] $[Os_2Br_9]^{3-}$** identified only from X-ray powder photography [Emerson & Fergusson 1983].

The **di-μ-bromobis[tetrabromoosmate(IV)]** $[Os_2Br_{10}]^{2-}$ anion has also been obtained, by heating $(NBu_4)_2[OsBr_6]$. The anion was isolated as a NBu_4^+ salt and was characterised by single crystal X-ray diffraction [Cotton et al. 1984]. The complex ion consists of an edge sharing bioctahedron with no evidence for Os-Os interaction. The Os-Br bridging bond lengths of 2.540(3) and 2.548(3) Å are longer than the Os-Br terminal bond lengths which lie in the range 2.441(4) - 2.460(4) Å.

8.3.4 Iodo- Complexes

Very few iodo- complexes have been isolated; a situation which is common for all four metals.

A) Hexaiodo- Complexes

The **hexaiodoosmate(IV)** $[OsI_6]^{2-}$ ion has been isolated as the Rb^+ and Cs^+ salts and they have the cubic $K_2[PtCl_6]$ structure [Brendel et al. 1985].

The $Co(en)_3^{3+}$ salt of **hexaiodoosmate(III)** $[OsI_6]^{3-}$ has also been reported and was made by reduction of $[OsI_6]^{2-}$ with silver metal [Campbell et al. 1985]

B) Pentaiodo- Complexes

Only two pentaiodo- complexes have been reported, **pentaiodo(carbonyl)osmate(III)** $[Os(CO)I_5]^{2-}$ [Johannsen & Preetz 1977] and **pentaiodo(nitrosyl)osmate(II)** $[Os(NO)I_5]^{2-}$ [Bol'shakov et al.

1972; Sinitsyn et al. 1975; Bol'shakov et al. 1976]. The carbonyl complex was produced from the bromo- complex by halogen exchange.

8.3.5 Mixed Halogeno- Complexes of Osmium

Preetz and coworkers have studied in detail the formation and reaction chemistry of mixed halogeno- complexes of osmium. The complexes were mainly prepared by halogen exchange in organic solvents. Many stereoisomers can be formed from systems such as $[OsX_nY_{6-n}]^{x-}$ and these were separated, using ion-exchange chromatography, ionophoresis or electrophoresis [Preetz & Petros 1975; Preetz & Shulka 1977; Shulka & Preetz 1979b; Shulka & Preetz 1979a; Preetz et al. 1984; Preetz & Groth 1986; Keller & Homborg 1976; Preetz & Nadler 1971; Preetz and Pfeifer 1967; Preetz & Homborg 1970; Jorgensen et al. 1971; Preetz & Walter 1971; Preetz & Walter 1973; Hasenpusch & Preetz 1977b; Preetz & Hasenpusch 1976; Preetz & Nadler 1974; Hasenpusch & Preetz 1977a; Barka & Preetz 1977; Preetz & Walter 1973; Preetz et al. 1973; Preetz et al. 1974; Preetz & Homborg 1974; Zerbe & Preetz 1982; Horns & Preetz 1986]

Complex	Os-X	Os-L	Os-Os	Ref.
$NaK[Os(NO)F_5].H_2O$	1.991(8) cis, 1.966(5) trans	1.707(9)		1
$Cs_2[Os(NO)F_5]$	1.986(9) cis, 1.947(5) trans	1.675(6)		1
$(NEt_4)[OsCl_6]$	2.295(3)-2.308(3)			2
$(PPh_4)[OsCl_6]$	2.273(3)-2.295(2)			3
$(PPh_4)_2[OsCl_6]$	2.325(3)-2.338(3)			3
$K_2[Os(N)Cl_5]$	2.359(4)-2.367(4) cis, 2.605(4) trans	1.614(13)		4
$(PPh_4)[Os(Am)Cl_5].CH_2Cl_2$	2.310(2)-2.348(2) cis, 2.279(3) trans	1.97(1)		5
$(PPN)_2[Os_2Cl_8]$	2.178(6)-2.357(6)		2.195(2)	6
$(NBu_4)_2[Os_2Cl_{10}]$	2.296(2)-2.308(2), 2.412(2) bridg.			2
$Cs_4[Os_2OCl_{10}]$	2.433(7) trans, 2.367(6)-2.375(6) cis	1.7777(15)		7
$(NBu_4)_2[Os_2Br_{10}]$	2.441(4)-2.460(4) term., 2.540(3), 2.548(3) bridg.			8

References

[1] Salomov et al. 1984 [2] Krebs et al. 1984 [3] Kim et al. 1984 [4] Bright & Ibers 1969 [5] Weber et al. 1982 [6] Fanwick et al. 1985 [7] Tebbe & von Schnering 1973 [8] Cotton et al. 1984

TABLE 8.2

Summary of structural data for osmium halogeno- complexes. Bond lengths in Å.

KEY

Am = $NC(CCl_3)NCCl(CCl_3)$
PPN = bis(triphenylphosphine)iminium

8.4 RHODIUM

8.4.1 Fluoro- Complexes

A) Hexafluoro- Complexes

A number of salts of the pentavalent rhodium species **hexafluororhodate(V)** $[RhF_6]^-$ have been prepared. Cations such as O_2^+ [Edwards et al. 1974] NO^+ [Sunder et al. 1979], alkali metal cations Na^+, K^+, Rb^+, and Cs^+ [Wilhelm & Hoppe 1976], and KrF^+ [Sokolov et al. 1976] have been used. The salts were made from either fluorination of the metal or $RhCl_3.xH_2O$, usually under high pressure. The K^+, Rb^+, and Cs^+ salts are hexagonal and have the $Ba[GeF_6]$ structure. The Na^+ salt is also hexagonal and has the $Li[SbF_6]$ structure.

The tetravalent rhodium species **hexafluororhodate(IV)** $[RhF_6]^{2-}$ is well characterised and many alkali metal and alkaline earth salts have been produced by methods similar to those used for the pentavalent salts [Pastukhova et al. 1972; Wilhelm & Hoppe 1974a; Wilhelm & Hoppe 1974b]. A silver(II) salt was similarly prepared [Muller & Hoppe 1972]. The NO^+ salt was produced by treating the oxygenyl salt $(O_2)[RhF_6]$ with NOF [Sunder et al. 1979]. The structures of many of these compounds were investigated using X-ray powder diffraction. The Ba^{2+} and Sr^{2+} salts are hexagonal and have the $Ba[SiF_6]$ structure [Wilhelm & Hoppe 1974b], whereas the Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Ni^{2+} salts are hexagonal and have the $Li[SbF_6]$ structure [Wilhelm & Hoppe 1974b].

The tervalent **hexafluororhodate(III)** $[RhF_6]^{3-}$ species has been prepared and salts of the type $CsA[RhF_6]$ for A = Mn^{2+}, Ni^{2+}, Zn^{2+},

Cu^{2+}, Pd^{2+} have been isolated [Jesse & Hoppe 1977a; Jesse & Hoppe 1977b; Jesse & Hoppe 1977c; Hoppe & Jesse 1973]. All the salts are cubic and have the $RbNi[CrF_6]$ structure.

Lithium salts of the type $LiA[RhF_6]$ for $A = M^{2+}$ have also been isolated [Grosse & Hoppe 1986; Viebahn & Epple 1976]. All the complexes where M = Mg, Co, Zn, and Cu are tetragonal, with the trirutile structure and space group $P4_2/mnm$. However the $LiMn^{3+}$, complex has the $Na_2[SiF_6]$ structure; space group P321, and the $LiCa^{3+}$ and $LiCd^{3+}$ complexes have the $Li_2[ZrF_6]$ structure with space group $P\bar{3}1c$.

The single crystal X-ray structure determination of the complex $(Pb_2F)[RhF_6]$ has been reported [Domesle & Hoppe 1983]. The fluorine atoms are coordinated to the rhodium in an octaherdal manner, and the Ru-F bond lengths all lie in the range 1.924(2) - 1.993(2) A. An analogous Sr_2F^{3+} complex, $(Sr_2F)[RhF_6]$ was found to be isostructural with the Pb_2F^{3+} complex [Domesle & Hoppe 1983].

B) Pentafluoro- Complexes

The only pentafluoro- species that has been reported is the **pentafluoro(aqua)rhodate(III)** $[Rh(H_2O)F_5]^{2-}$ ion, formed from the aquation of $K_3[RhF_6]$ [Shipachev et al. 1980].

8.4.2 Chloro- Complexes

A) Hexachloro- Complexes

Only one hexachloro- salt of rhodium(IV) has been isolated. The caesium salt of the **hexachlororhodate(IV)** $[RhCl_6]^{2-}$ ion has been

obtained by chlorination of $Cs_3[RhCl_6]$ [Griffith 1967]. The compound is unstable and rapidly reduced to rhodium(III). It is reported to be isostructural with $(NH_4)_2[PtCl_6]$. No new preparative or structural work has been done since 1967.

In contrast to rhodium(IV), the chloro- complexes of rhodium(III) are well characterised and stable. The tervalent **hexachlororhodate(III)** $[RhCl_6]^{3-}$ anion has been isolated with several cations including alkali metal cations, NH_4^+, and NMe_4^+ [Fergusson & Sherlock 1977; Treiber et al. 1986; Krause et al. 1982; Walewski & Dobrowolski 1979; Krylov et al. 1983]. Several organoamine salts have also been reported [Spacu & Gheorghui 1968; Bondarenko et al. 1971; Zipp and Madan 1975]. The salts were made from $RhCl_3.xH_2O$ or by metathetical replacement of the cation.

The X-ray powder diffraction pattern of the K^+ salt showed that it was isomorphous with the iridium and ruthenium analogues [Krylov & Stepareva 1985] and with the Rb^+ salt [Fergusson & Sherlock 1977]. The Cs^+ salt has however a different structure to all of these complexes. The monohydrate complex $K_3[RhCl_6].H_2O$ was found to be isomorphous with the iridium analogue with space group Pbcn [Fergusson & Sherlock 1977]. The complexes $(NH_4)_3[RhCl_6].H_2O$ and $Rb_3[RhCl_6].H_2O$ are isomorphous with each other and with the iridium salt $Rb_3[IrCl_6].H_2O$ and have the space group Pnma or $Pna2_1$ [Fergusson & Sherlock 1977]. The Cs^+ salt $Cs_3[RhCl_6].H_2O$ was isomorphous with the analogous iridium complex.

The single crystal X-ray structure of $K_3[RhCl_6].H_2O$ has been reported [Cresswell et al. 1972; Murray-Rust & Murray-Rust 1975], and the complex is orthorhombic space group Pbcn. No molecular symmetry was required by the space group, and the structure was found to

consist of octahedral $[RhCl_6]^{3-}$ units with six independant Rh-Cl bond lengths which lie in the range 2.302(4) - 2.366(4) Å.

The single crystal X-ray structure has also been carried out on the complex $(NH_4)_3[RhCl_6].H_2O$ [Treiber et al. 1986]. The complex belongs to the orthorhombic crystal system with space group Pnma. The chlorine atoms are coordinated in an octahedral manner to the rhodium, and there are four independant Rh-Cl bond lengths in the range 2.340(2) - 2.361(3) Å. There is some evidence of hydrogen bonding between the water moleules and the ammonium cation.

B) Pentachloro- Complexes

All the pentachloro- complexes of rhodium are tervalent. The **pentachloro(acetonitrile)rhodate(III)** $[Rh(CH_3CN)Cl_5]^{3-}$ anion has been isolated with Cs^+, NH_4^+ and NMe_4^+ cations. They were produced from the sodium salt in a 1:1 mixture of water and acetonitrile [Catsikis & Good 1969]. The Na^+ salt was obtained by extracting $Na_3[RhCl_6]$ from an aqueous solution with acetonitrile.

The **pentachloro(aqua)rhodate(III)** $[Rh(H_2O)Cl_5]^{2-}$ is well characterised and can be made by the aquation of a number of Ru(III) species such as $A_3[RhCl_6].H_2O$, $RhCl_3.xH_2O$, and $H_3[RhCl_6]$ [Fergusson & Sherlock 1977; Bugli 1981; Thomas & Stanko 1973; Work & Good 1970; Belyaev & Fedotov 1983; Belyaev et al. 1984; Treiber et al. 1986; Spacu & Gheorghiu 1968].

The X-ray powder diffractograms showed that the K^+, Rb^+, and NH_4^+ salts were all isomorphous, whereas the Cs^+ salt was isomorphous with the analogous salts of Cr, Fe, and Ru [Fergusson & Sherlock 1977].

The single crystal X-ray structures have been determined for the Cs^+ and the NH_4^+ salts. Although both structures belong to the orthorhombic crystal system, they are not isomorphous. The NH_4^+ salt crystallised out with space group Pnma [Bugli & Potvin 1981], and the Cs^+ salt with space group Amam [Thomas & Stanko 1973]. The molecular structures were similar with octahedral coordination around the rhodium of five chlorine atoms and one water molecule. In both complexes the Rh-Cl bond length for the Cl atom trans to the oxygen atom was shortened; 2.304(2) Å and 2.300(5) Å for the NH_4^+ and Cs^+ salts respectively, compared with the other Rh-Cl bond lengths which were found to be in the range 2.337(2) - 2.356(2) Å for the NH_4^+ salt, and the single length of 2.337(3) Å for the Cs^+ salt. The Rh-O bond lengths of 2.090(6) Å and 2.096(13) Å for NH_4^+ and Cs^+ salts were found to be relatively long compared with other Rh-O bond lengths.

The complex anion **pentachloro(diethylether)rhodate(III)** $[Rh(Et_2O)Cl_5]^{2-}$ has been isolated as the acid $H_2[Rh(Et_2O)Cl_5].3Et_2O$. It was formed by mixing $RhCl_3.xH_2O$ and Et_2O [Galinos et al. 1972].

The **pentachloro(carbonyl)rhodate(III)** $[Rh(CO)Cl_5]^{2-}$ ion has been isolated with several cations and was made by treating Rh(III) species or $[Rh(CO)_2Cl]_2$ with formic acid or CO [Stanko et al. 1969; Cleare & Griffith 1969; Colton et al. 1970; Forster 1969]. The X-ray powder diffractogram showed that the NEt_4^+ salt was isostructural with the iodo- analogue [Dahm & Forster 1970] and belongs to the cubic crystal system with space group Fm3m and the $K_2[PtCl_6]$ structure. The Cs^+ salt is isomorphous with the Ru analogue [Stanko et al. 1969].

The tervalent **pentachloro(sulphamato)rhodate(III)** $[Rh(NH_2SO_3)Cl_5]^{3-}$ species was obtained as the sodium salt by treating $Na_3[RhCl_6].xH_2O$ with sulphamic acid. The infrared spectrum indicated

that the sulphamato ligand was nitrogen bound [Griffith & Pawson 1973a].

C) Dimetallic Complexes

The dimeric species **tri-μ-chlorobis[trichlororhodate(III)** $[Rh_2Cl_9]^{3-}$ has been reported associated with a number cations, alkali metal cations NMe_4^+, NEt_4^+ [Fergusson & Sherlock 1977; Work & Good 1970; Krylov & Stepareva 1985], $N(CH_3)_3Ph^+$ [Cotton & Ucko 1972].

The X-ray powder diffraction patterns of the K^+, NH_4^+, Rb^+, Cs^+, NMe_4^+, and NEt_4^+ salts were indexed on the basis of a hexagonal cell [Fergusson & Sherlock 1977], and the M-M distance was calculated. The presence of a Rh-Rh bond was investigated by determining the single crystal X-ray structure of the trimethylphenylammonium salt [Cotton & Ucko 1972]. Unfortunately the structure analysis was unable to be fully refined. A large orthorhombic unit cell was found but intial attempts at the structure solution indicated that the cell possessed psuedosymmetry along the z axis. The final solution was performed using a cell with 1/3 of the length of the original z axis. The structure was solved in the space group Pnma and the anion was found to consist of a confacial bioctahedra with near ideal D_{3h} symmetry. The Rh-Rh distance was found to be 3.121(5) Å and the anion was distorted in such a manner that it appeared that some repulsion existed between the rhodium atoms. The Bridging Rh-Cl bond lengths lay in the range 2.391(9) - 2.442(12) Å, significantly longer than the terminal Rh-Cl bond lengths of 2.227(11) - 2.310(14) Å.

8.4.3 Bromo- Complexes

A) Hexabromo- Complexes

The hexabromo- complexes are less well characterised for rhodium than for ruthenium or osmium. The **hexabromorhodate(III)** $[RhBr_6]^{3-}$ ion has been isolated as the K^+ salt from the chloro- analogue $K_3[RhCl_6]$ [Robb & Bekker 1973], and as the amine salt $N(CH_2CH_2NH_3)_3^{3+}$ [Zipp & Madan 1975].

B) Pentabromo- Complexes

Little work has been done on pentabromo- complexes of rhodium. The **pentabromo(aqua)rhodate(III)** $[Rh(H_2O)Br_5]^{2-}$ ion is known [Robb & Bekker 1973] as is the **pentabromo(carbonyl)rhodate(III)** $[Rh(CO)Br_5]^{2-}$ ion. The K^+ salt was obtained for the aqua species and the Cs^+, and NEt_4^+ salts isolated for the carbonyl complex [Cleare & Griffith 1969; Colton et al. 1970; Forster 1969]. The aqua complex was prepared from $Ru(OH)_3(H_2O)_3$ and KBr/HBr, and the carbonyl complex from Rh(III) and formic acid or from rhodium carbonyl chloride. Dahm and Forster (1970) found that the NEt_4^+ salt was isomorphous with the iodo- analogue and has the $K_2[PtCl_6]$ structure.

C) Dimetallic Complexes

The triply bridged **tri-μ-bromobis[tribromorhodate(III)]** $[Rh_2Br_9]^{3-}$ ion, and the doubly bridged **di-μ-bromobis[tetrabromorhodate(III)]** $[Rh_2Br_{10}]^{4-}$ ion are known, and were made by dimerisation reactions of hexabromo- complexes [Fergusson

& Sherlock 1877; Robb & Becker 1973]. The $[Rh_2Br_9]^{3-}$ ion is the better characterised of the two, and has been isolated as the K^+, Rb^+, Cs^+ and alkylammonium salts. The $[Rh_2Br_{10}]^{4-}$ ion has only been isolated as the K^+ salt [Robb & Becker 1973].

8.4.4 Iodo- Complexes

A) Hexaiodo- Complexes

The only known hexaiodo- complex for rhodium is the trivalent **hexaiodorhodate(III)** $[RhI_6]^{3-}$ species which was isolated as the diantipyrilmethane salt $(C_{23}H_{24}O_2N_4H)_3[RhI_6]$ by the addition of diantipyrilmethane to $RhCl_3 \cdot xH_2O$ in the presence of KI [Pilipenko & Ol'khovich 1968].

B) Pentaiodo- Complexes

The **pentaiodo(carbonyl)rhodate(III)** $[Rh(CO)I_5]^{2-}$ ion, isolated as the Cs^+ and NEt_4^+ salts, is the only pentaiodo- complex of rhodium(III) reported [Colton et al. 1970; Forster 1969].

The single crystal X-ray structure of the NEt_4^+ salt was partially solved by Dahm and Forster (1970). The complex which belongs to the cubic crystal system and was solved in the space group Fm3m. The Rh atom has crystallographically imposed octahedral symmetry, and thus there is disorder in the structure. A bond length of 2.64 Å was reported.

C) Dimetallic Complexes

The dimeric complex **di-μ-iodobis[tetraiodorhodate(III)]** $[Rh_2I_{10}]^{4-}$ was isolated as the Cs^+ salt from treating and aging a solution of $RhCl_3 \cdot xH_2O$ and $KI/CsNO_3$ [Stella & DiCasa 1971].

Complex	Rh-X	Rh-L	Ref.
$(Pb_2F)[RhF_6]$	1.924(2)-1.993(2)		1
$K_3[RhCl_6].H_2O$	2.302(4)-2.366(4)		2
$(NH_4)_3[RhCl_6].H_2O$	2.340(2)-2.361(3)		3
$Cs_2[Rh(H_2O)Cl_5]$	2.337(3) cis, 2.300(5) trans	2.096(13)	4
$(NH_4)_2[Rh(H_2O)Cl_5]$	2.337(2)-2.356(2) cis, 2.304(2) trans	2.090(6)	5
$(NMe_3Ph)_3[Rh_2Cl_9]$	2.227(11)-2.310(14), 2.391(9)-2.442(12) bridg.		6
$(NEt_4)_2[Rh(CO)I_5]$	2.64		7

References

[1] Domesle & Hoppe 1983 [2] Cresswell et al. 1972; Murray-Rust & Murray-Rust 1975 [3] Treiber et al. 1986 [4] Thomas & Stanko 1973 [5] Bugli & Potvin 1981 [6] Cotton & Ucko (1972)[7] Dahm & Forster 1970.

TABLE 8.3

Summary of structural data for rhodium halogeno- complexes. Bond lengths in Å.

8.5 IRIDIUM

Of the four metals reviewed, the halogeno- chemistry of irdium is least well developed. This is somewhat surprising in view of the accessibility of the tetra- and tervalent oxidation states. The high cost of irdium may be a factor, also iridium is the least abundant of the four metals. The mean crustal abundances are: Ru 0.001; Rh, 0.0002; Os 0.0001; and Ir 0.000003 mg kg^{-1} [Bowen 1979].

8.5.1 Fluoro- Complexes

A) Hexafluoro- Complexes

Like the other metals the pentavalent ion **hexafluoroiridate(V)** $[IrF_6]^-$ is known, and has been isolated with some unusual cations; NO^+, BrF_2^+, H_3O^+, C_8^+, NO_2^+, XeF^+ and $Xe_2F_3^+$ [Griffiths & Sunder 1975; Sunder et al. 1979; Sladky et al. 1969; Bartlett et al. 1978a; Bartlett et al. 1980; Selig et al. 1978; Mit'kin et al. 1983]. A potassium salt is also known [Burns & O'Donnell 1980a]. The complexes were prepared in a similar manner as described for osmium.

The **hexafluoroiridate(IV)** $[IrF_6]^{2-}$ ion has been obtained as the NO^+ salt [Griffiths & Sunder 1975; Sunder et al. 1979] and the K^+ salt [Preetz & Petros 1971].

The **hexafluoroiridate(III)** $[IrF_6]^{3-}$ ion occurs as the K^+, Rb^+, and Cs^+ salts made from the reduction of $[IrF_6]^{2-}$ with hydrazine [Zemskov et al. 1977a]. The K^+ and Rb^+ salts both have the cubic $K_2[PtCl_6]$ structure.

B) Dimetallic Complexes

The only reported dimeric fluoro- complex is the **μ-fluorobis[pentafluoroiridate(V)]** $[Ir_2F_{11}]^-$ ion, which has been isolated as the XeF^+ salt from treating IrF_5 and XeF_2 in BrF_5 [Sladky et al. 1969].

8.5.2 Chloro- Complexes

A) Hexachloro- Complexes

The $[IrCl_6]^{2-}$ ion is best obtained from chlorination of the metal at elevated temperatures in the presence of KCl. The alkali metal salts of the tetravalent ion **hexachloroiridate(IV)** $[IrCl_6]^{2-}$ are known, prepared from ion exchange with the K^+ salt or acid [Fergusson & Rankin 1983; Brouwer et al. 1974], and several organoamine salts [Spacu & Gheorghui 1969; Pannetier et al. 1970; Craciunescu et al. 1974; Birnbaum 1969] have also been isolated from the acid or by extraction of the ion from organic solvents [Bol'shakov et al. 1974]. The intercalated graphite salt $C_8[IrCl_6]$ is also known [Stumpp et al. 1985]. The alkali metal salts are all cubic and have the $K_2[PtCl_6]$ structure [Brown et al. 1967].

Several salts of the tervalent **hexachloroiridate(III)** $[IrCl_6]^{3-}$ ion are known and were prepared by cation exchange as for the tetravalent salts [Fergusson & Rankin 1983; Birnbaum 1969; Gheorghui 1969]. The ion is usually produced by reduction of $[IrCl_6]^{2-}$ using $FeSO_4$ [Kukushikin & Soboleva 1970], oxalate [Fergusson & Rankin 1983], or organoamines [Birnbaum 1970]. Some salts obtained with large cations were formed by reaction with other Ir(III) species [Zipp &

Madan 1975; Baranovskii et al. 1970; Galsbol & Rasmussen 1982; Sinitsyn et al. 1985b; Galsbol 1974; Fergusson & Rankin 1983]. The complex $Na_3[IrCl_6].10H_2O$ crystallises in the rhombohedral crystal system with space group $R\bar{3}m$ [Pannetier et al. 1972]. The monohydrate NH_4^+ and K^+ salts are orthorhombic [Rankin et al. 1983]. and there is octahedral coordination around the metal. The Ir-Cl bond lengths lie in the range 2.336(3) - 2.387(3) Å for both salts. The single crystal X-ray structure of the anhydrous K^+, originally reported to be triclinic [Rankin et al. 1983], is in fact monoclinic $P2_1/c$ [Coll et al. 1987a], and the Ir-Cl bond lengths for the octahedrally coordinated complex lie in the range 2.352(5) - 2.373(4) Å.

B) Pentachloro- Complexes

The majority of the pentachloro- complexes of iridium of the type $A_n[Ir(L)Cl_5]$ are tervalent and contain a neutral sixth ligand; for example L = H_2O, CH_3CN, CO, SPh_2, NH_2SO_3, NO^+ or an organoamine. However, one tetravalent complex anion has been reported **pentachloro(aqua)iridate(IV)** $[Ir(H_2O)Cl_6]^-$ but this was only characterised in solution when Ir(III) species were irradiated [Moggi et al. 1970; Nikol'skii & Popov 1980].

The tervalent complex anions were mostly made from Ir(III) species such as $IrCl_3.xH_2O$, $A_2[Ir(H_2O)Cl_5]$, and $A_3[IrCl_6]$ by methods similar to those reported for the other platinum metals [Catsikis & Good 1973; Sinitsyn et al. 1982a; Fergusson & Rankin 1983; Birbaum 1970; Gheorghui 1969; Cleare & Griffith 1969; Cleare & Griffith 1967; Cleare 1967; Canziani et al. 1983; Forster 1971; Dahm & Forster 1970; Gulliver et al. 1980; Lareze & Sebagh 1970; Lareze & Bokobza-Sebagh

1973; Griffith & Pawson 1973a; Moggi et al. 1970; Lareze 1976; Zipp & Madan 1975].

The single crystal X-ray structure determination of $K[Ir(NO)Cl_5].H_2O$ has been reported [Bottomley 1975]. As seen for other similar complexes coordination around the metal is octahedral, with the trans Ir-Cl bond length shorter (2.286(3) Å) than the cis Ir-Cl bond lengths which were 2.335(2) and 2.342(2) Å.

The single crystal X-ray structure of $K_2[Ir(C_6H_4N_2)Cl_5].1/2H_2O$ has been reported [Bonnet & Jeannin 1973], and has octahedral coordination around the metal, with only slight distortions from ideal symmtery. The cis Ir-Cl bond lengths were all in the range 2.339(3) - 2.357(2) Å, whereas the Ir-Cl bond trans to the pyrazine ligand was longer at 2.379(2) Å. The pyrazine ligand was bound through the nitrogen atom with an Ir-N bond length of 2.016(3) Å.

C) Dimetallic Complexes

Four dimetallic complexes are known; **tri-μ-chlorobis[trichloroiridate(III)]** $[Ir_2Cl_9]^{3-}$ isolated as K^+, Rb^+, Cs^+ and NMe_4^+ salts [Fergusson & Rankin 1983; Steinebach & Preetz 1985], **di-μ-chlorobis[tetrachloroiridate(III)]** $[Ir_2Cl_{10}]^{4-}$, as the K^+ salt [Sinitsyn et al. 1982a], and two complexes in which pyridine bridges the metal atoms, tetravalent **di-μ-pyridinebis[pentachloroiridate(IV)]** $[Ir_2(Pyr)Cl_{10}]^{2-}$ (as the K^+ salt) and tervalent **di-μ-pyridinebis[pentachloroiridate(III)]** $[Ir_2(Pyr)Cl_{10}]^{4-}$ as the Cs^+ salt [Lareze 1976]. The tervalent salts were made by achieving dimerisation of the monometallic complexes

$A_n[Ir(H_2O)Cl_5]$ or $A_3[IrCl_6]$. The tetravalent complex was produced by oxidation of the tervalent complex $Cs_4[Ir_2(Pyr)Cl_{10}]$ with HNO_3.

8.5.3 Bromo- Complexes

A) Hexabromo- Complexes

The tetravalent species **hexabromoiridate(IV)** $[IrBr_6]^{2-}$ has been well characterised and the alkali metal salts are known [Fergusson & Rankin 1983; Dury & Dekorte 1983]. Normally these are prepared from the chloro- analogues by oxidation of the tervalent bromo- or chloro- species. The single crystal X-ray structure determinations have been reported for the NH_4^+ and H_3O^+ salts and both belong to the cubic crystal system with space group Fm3m, and have the $K_2[PtCl_6]$ structure [Coll et al. 1987b]. The Ir-Br lengths were 2.515(1) and 2.549(3) Å respectively which are similar in length to bromo- complexes of iridium(III). The K^+, Rb^+, and Cs^+ are all cubic with the $K_2[PtCl_6]$ structure [Brown et al. 1967]

The tervalent ion **hexabromoiridate(III)** $[IrBr_6]^{3-}$ is less well characterised and unstable with respect to oxidation to Ir(IV). Most salts only exist with large cations [Zipp & Madan 1975; Fergusson & Rankin 1983]. The single crystal X-ray structure has been reported for $Rb_3[IrBr_6].H_2O$ [Rankin et al. 1983] and the bromine atoms are coordinated to the iridium in an octahedral manner with four independant Ir-Br bond lengths which lie in the range 2.497(5) - 2.512(4) Å. The NH_4^+ and Cs^+ salts were found to be isostructural with the Rb^+ salt [Rankin et al. 1983].

B) Pentabromo- Complexes

The only reported pentabromo- complexes are the Cs^+ and NEt_4^+ salts of the tervalent **pentabromo(carbonyl)iridate(III)** $[Ir(CO)Br_5]^{2-}$ ion [Cleare & Griffith 1969; Cleare & Griffith 1967; Cleare 1967; Forster 1971], and the K^+ salt of the **pentabromo(nitrosyl)iridate(III)** $[Ir(NO)Br_5]^-$ ion [Bottomley 1975]. The single crystal X-ray structure has been reported for the nitrosyl complex [Bottomley 1975], and it was found to be isostructural with the chloro- analogue. The five bromine atoms and NO group are coordinated in an octahedral manner to the metal and the anion has only small deviations from ideal C_s symmetry. As has been reported for other similar halogeno- nitrosyl complexes, the bond length trans to the NO group is short. The Ir-Br trans bond length is 2.419(4) Å and Ir-Br cis bond lengths were 2.475(3) and 2.485(3) Å.

C) Dimetallic Complexes

The only dimetallic complex anion reported is the **tri-μ-bromobis[tribromoiridate(III)]** $[Ir_2Br_9]^{3-}$ species which has been isolated as the Rb^+, Cs^+ NMe_4^+, and NBu_4^+ salts. The complexes were isolated by dimerisation of Ir(III) bromo- species [Fergusson & Rankin 1983; Steinebach & Preetz 1985].

8.5.4 Iodo- Complexes

A) Hexaiodo- Complexes

The only reported hexaiodo- complex is the Cs^+ salt of **hexaiodoiridate(III)** $[IrI_6]^{3-}$ made by tempering $Cs_3[IrBr_6]$ and NaI [Preetz & Steinebach 1986].

B) Pentaiodo- Complexes

The only reported pentaiodo- complex is the NEt_4^+ salt of **pentabromo(carbonyl)iridate(III)** $[Ir(CO)I_5]^{2-}$ [Forster 1971]. It is isostructural with the analogous rhodium salt which has the cubic $K_2[PtCl_6]$ structure [Dahm & Forster 1970].

8.5.5 Mixed Halogeno- Complexes of Iridium

Preetz and coworkers have prepared several mixed halogeno- complexes of iridium, but the chemistry is not as well developed as for osmium [Preetz & Tensfeldt 1985; Tensfeldt & Preetz 1984; Preetz & Nadler 1971; Preetz & Steinebach 1985; Preetz & Pfeifer 1967]. In the same way as for osmium the mixed halogeno- complexes were obtained by exchange reactions, and the isomers separated using ion-exchange chromatography or electrophoresis.

Complex	Ir-X	Ir-L	Ref.
$K_3[IrCl_6].H_2O$	2.336(3)-2.387(3)		1
$(NH_4)_3[IrCl_6].H_2O$	2.354(2)-2.380(2)		1
$K_3[IrCl_6]$	2.352(5)-2.373(4)		1, 2
$K[Ir(NO)Cl_5].H_2O$	2.335(2)-2.342(2) cis, 2.286(3) trans	1.760(11)	3
$K_2[Ir(C_6H_4N_2)Cl_5].1/2H_2O$	2.339(3)-2.357(2) cis, 2.379(2) trans	2.016(3)	4
$(H_3O)_2[IrBr_6]$	2.515(1)		5
$(NH_4)_2[IrBr_6]$	2.549(3)		5
$Rb_3[IrBr_6].H_2O$	2.497(5)-2.512(4)		1
$K[Ir(NO)Br_5].H_2O$	2.475(3),2.485(3) cis, 2.419(4) trans	1.710(25)	3

References

[1] Rankin et al. 1983 [2] Coll et al. 1987a [3] Bottomley 1975 [4] Bonnet & Jeanin 1973 [5] Coll et al. 1987b

TABLE 8.4

Summary of structural data for iridium halogeno- complexes. Bond lengths in Å.

8.6 SUMMARY

8.6.1 Structural Data

The structural data for the halogeno- complexes of the four platinum metals is summarised in Table 8.5 and allows for some generalisations.

Since the metallic radii of the four metals is similar; Ru 1.34 Å, Rh 1.34 Å, Os 1.35 Å, Ir 1.36 Å [Wells 1984], the metal-halogen bond length for the same oxidation state is expected to be quite similar also. This is observed from the values of the bond lengths for example; Rh(III)-Cl = 2.33 Å, Ir(III)-Cl = 2.36 Å and Ru(IV)-Cl = 2.33 Å, Os(IV)-Cl = 2.33 Å. There is some variation in M-X bond length when the halogen is opposite NO or N^{3-}, or bridges between two metal atoms. The M-X bond length for the halogen opposite NO is shortened for all the halogens (Tables 8.1 - 8.4).

A general lengthening of the M-X bond length is observed as the oxidation state of the metal decreases. This may be due to the decrease in the effective charge associated with the transition metal cation.

8.6.2 Principal Oxidation States for the Metals

There is some variation in the principal oxidation states for the halogeno- complexes of the platinum metals. The most stable oxidation state for ruthenium appears to be the tetravalent oxidation state, although the tervalent oxidation state is also stable especially for pentahalogeno- complexes. Osmium resembles ruthenium and similar complexes are known. Like ruthenium, the tetravalent oxidation state

	Oxidation State				
	VI	V	IV	III	II
F		Ru: 1.83		Rh: 1.96	Ru: 1.96 Os: 1.98
Cl	Os: 2.36	Os: 2.30	Ru: 2.33 Os: 2.33	Ru: 2.38 Rh: 2.33 Ir: 2.36	Ru: 2.37
Br			Os: 2.45 Ir: 2.42	Ru: 2.51 Ir: 2.50	
I				Rh: 2.64	

TABLE 8.5

Mid-point M-X bond lengths (Å) for platinum metal halogeno- complexes; excluding trans bonds in $A_n[M(L)X_5]$ complexes, and bridging bonds.

is stable, but the tervalent oxidation state is quite unstable with oxidation to Os(IV) occurring readily for the hexahalogeno- complexes. Although the tetravalent oxidation state is known for rhodium, the tervalent oxidation state is much more stable. However, for iridium the tervalent oxidation state is less stable with oxidation to the tetravalent oxidation state occurring easily.

When the sixth ligand is not a halogen, it is quite significant in its ability to stabilise certain oxidation states. In particular the nitrosyl and carbonyl ligands stabilise lower oxidation states (e.g. Os(III) or Ru(III)) and N^{3-} stabilises higher oxidation states. This effect is likely to be due to the different bonding characteristic of the ligands. For example the NO group is a good π-acceptor ligand, whereas the N^{3-} ligand is a strong σ-donor. The halogen also has an effect in stabilising certain oxidation states. Fluorine stabilises higher oxidation states, except when associated with say NO. Chlorine and bromine may occur in a high oxidation state if associated with an appropriate ligand such as N^{3-}, but along with iodine tend to favour lower oxidation states.

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CHAPTER 9

THE PREPARATIVE, STRUCTURAL, AND REACTION CHEMISTRIES OF PLATINUM METAL HALOGENO- COMPLEXES

9.1 INTRODUCTION

In this section of the thesis two areas were studied; the X-ray structural chemistry of some hexahalogenometallates was reinvestigated, and the preparation of some iridium(III) and rhodium(III) complexes with trichlorostannato- ligands was studied. The preparations were not straight forward, particularly for iridium, where oxidation occurred readily.

9.2 THE PREPARATION AND STRUCTURAL CHEMISTRY OF PLATINUM METAL HALGENO- COMPLEXES

9.2.1 An Investigation of the Structures of Hexahalogenometallates(III)

Rankin (1978) prepared and investigated a series of complexes of iridium of the general form $A_2[IrX_6]$, $A_3[IrX_6]$, and $A_3[IrX_6].xH_2O$. The complexes were investigated using X-ray diffraction, NQR, and Raman spectroscopy [Rankin et al. 1983]. In the present work some of the structural studies carried out by Rankin were reinvestigated; in particular the complexes $K_3[IrCl_6]$, $(NH_4)_3[IrCl_6]$, $K_3[RuCl_6]$, and $K_3[RhCl_6]$ were studied. Rankin had determined the single crystal X-ray structure of $K_3[IrCl_6]$, and on the basis of X-ray powder photography, and some X-ray single crystal precession photography concluded that the K^+ and NH_4^+ salts were isomorphous. Comments by a

referee indicated that the structure solution for $K_3[IrCl_6]$ was based on an incorrect space group assignment and so this complex was prepared and its X-ray structure redetermined. The results of the X-ray structure redetermination are described in Chapter 10. Although the crystallographic details of the structure are different, the molecular structure is quite similar to that found by Rankin. The X-ray powder patterns for all the above complexes were measured and although some of the patterns are similar, the complexes cannot be described as isomorphous (Figures 9.1 - 9.4). The X-ray powder diffractograms of $K_3[IrCl_6]$ and $K_3[RhCl_6]$ are similar but both are quite different to that of the others. Attempts to prepare crystals of $(NH_4)_3[IrCl_6]$, $K_3[RuCl_6]$, and $K_3[RhCl_6]$ of suitable quality for X-ray single crystal analysis were unsuccessful. However, the complex $(NH_4)_3[IrCl_6]$ was investigated by precession photography and found to belong to the orthorhombic crystal system (Chapter 10).

The tervalent metal halogeno- complexes with stoichiometries $A_3[MX_6]$, $A_2[MCl_5(H_2O)]$ and $A_3[M_2X_9]$ crystallise in a small number of recognised structural types [Coll et al. 1987b; Rankin et al. 1983; Emerson & Fergusson 1983; Fergusson & Greenaway 1978; Fergusson & Rankin 1983; Fergusson & Sherlock 1977; Griffith 1967; Seddon & Seddon 1984], and it is perhaps surprising that the complexes studied here crystallise out in different structures. The cation size appears to have an influence on the structure, and commonly the large cation caesium halogeno- complexes have different structures to the salts of smaller cations such as K^+, or NH_4^+ [Coll et al. 1987b]. If there is a large difference in the radius ratio r_{cation}/r_{anion} for two complexes, then there is frequently a difference in the structure [Rankin et al. 1983]. However, there is not much difference in cation

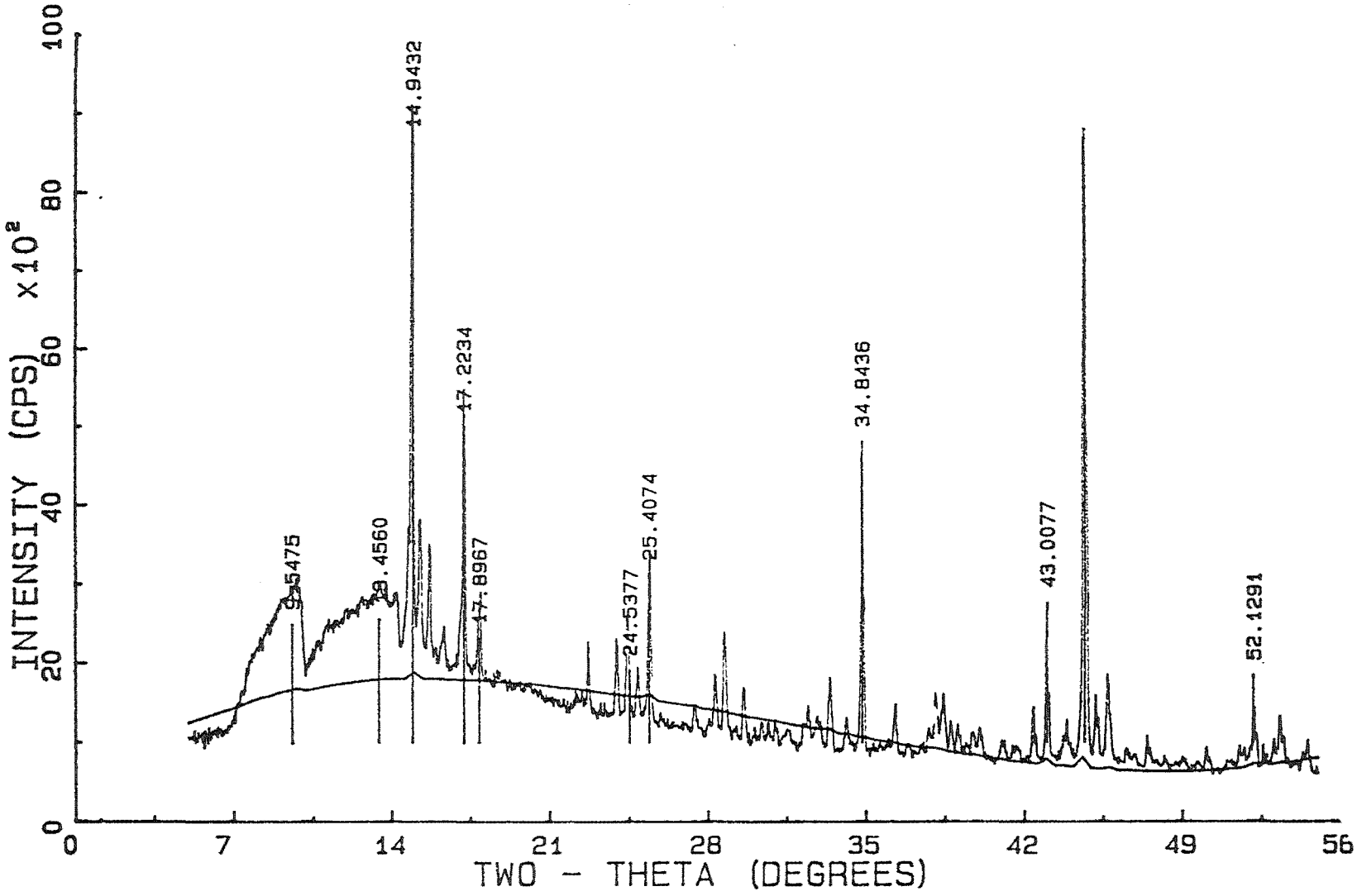


FIGURE 9.1

X-ray powder diffraction pattern of $K_3[IrCl_6]$

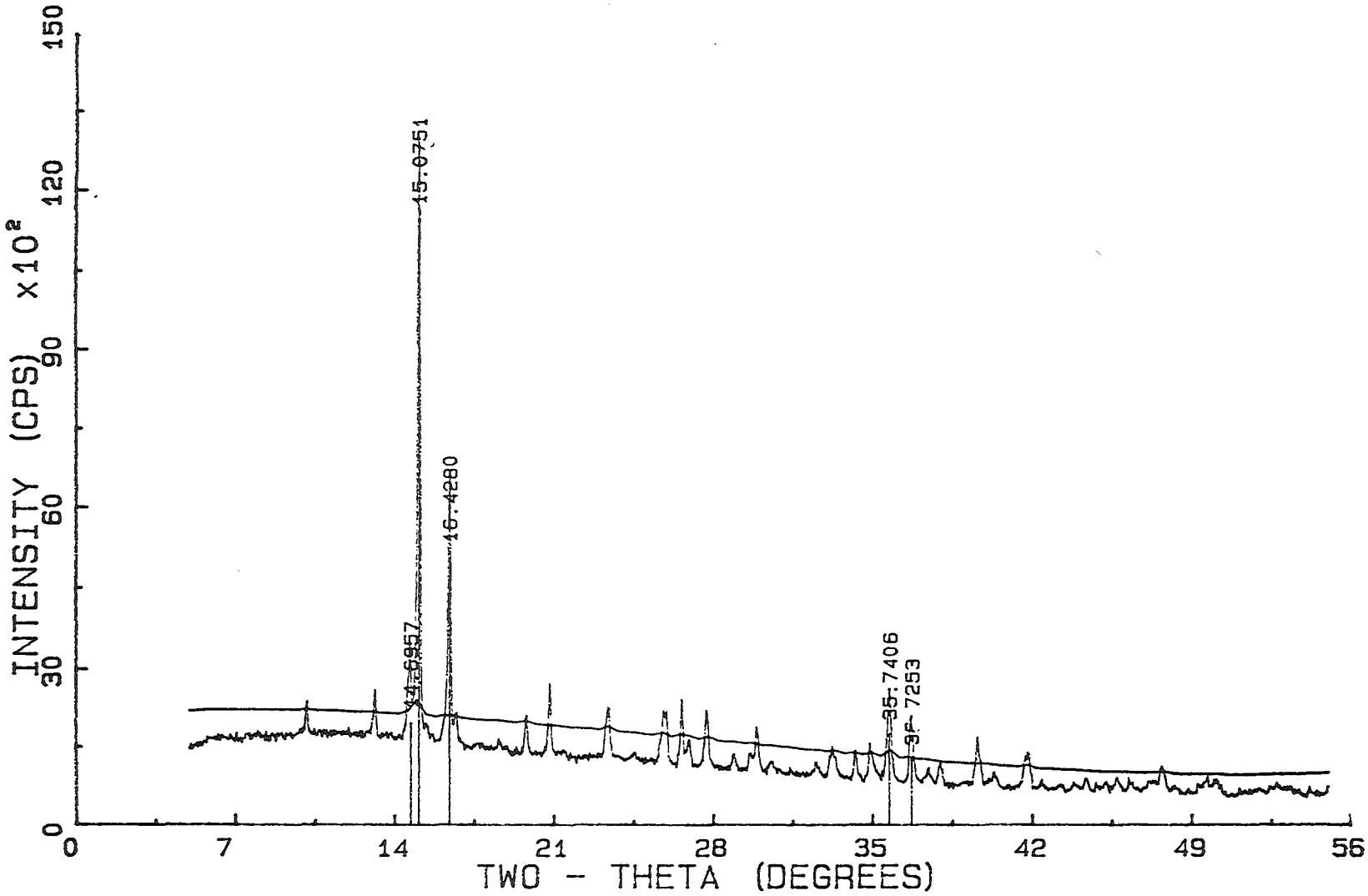


FIGURE 9.2

X-ray powder diffraction pattern of $(NH_4)_3[IrCl_6]$

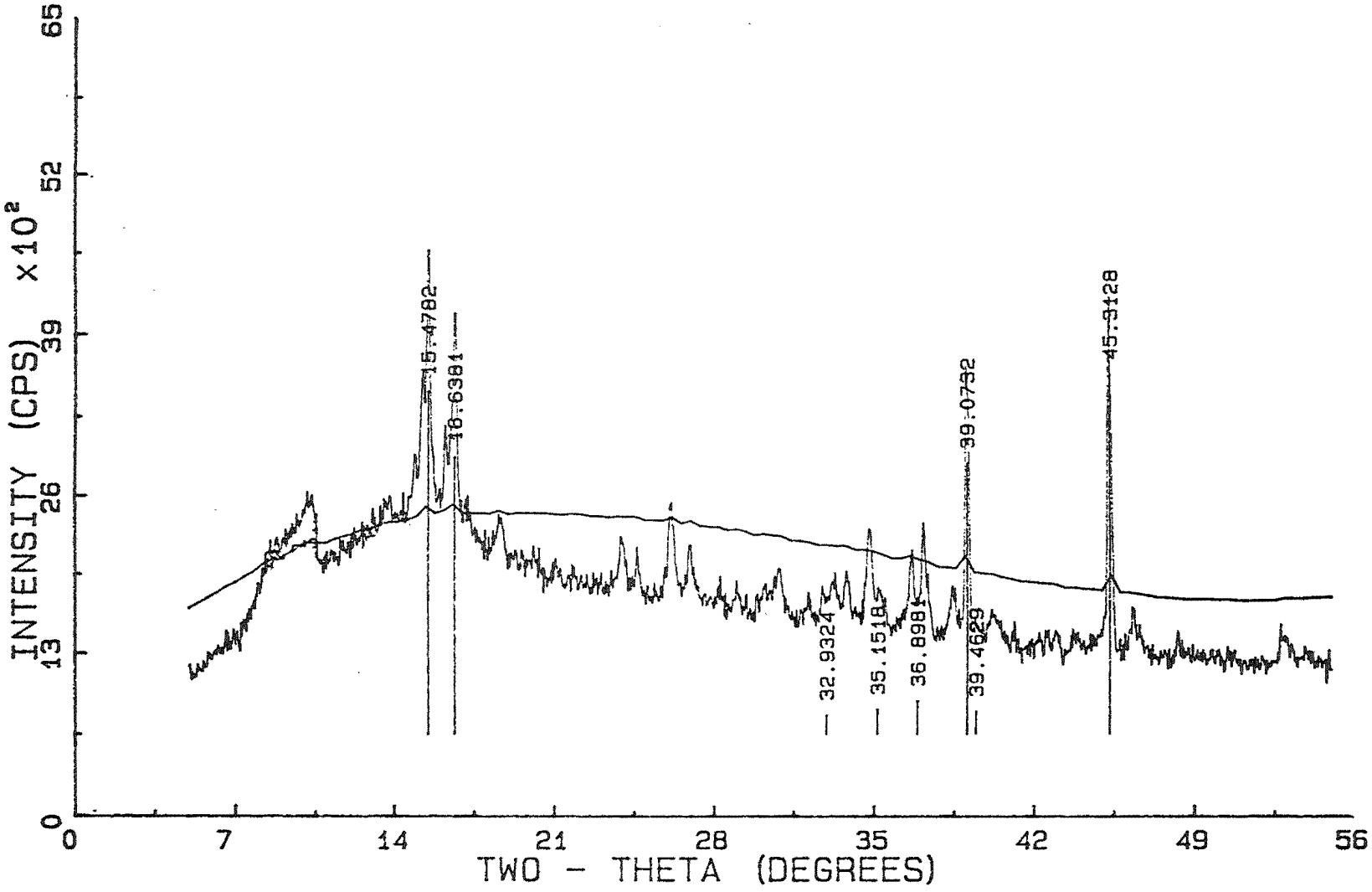


FIGURE 9.3

X-ray powder diffraction pattern of $K_3[RhCl_6]$

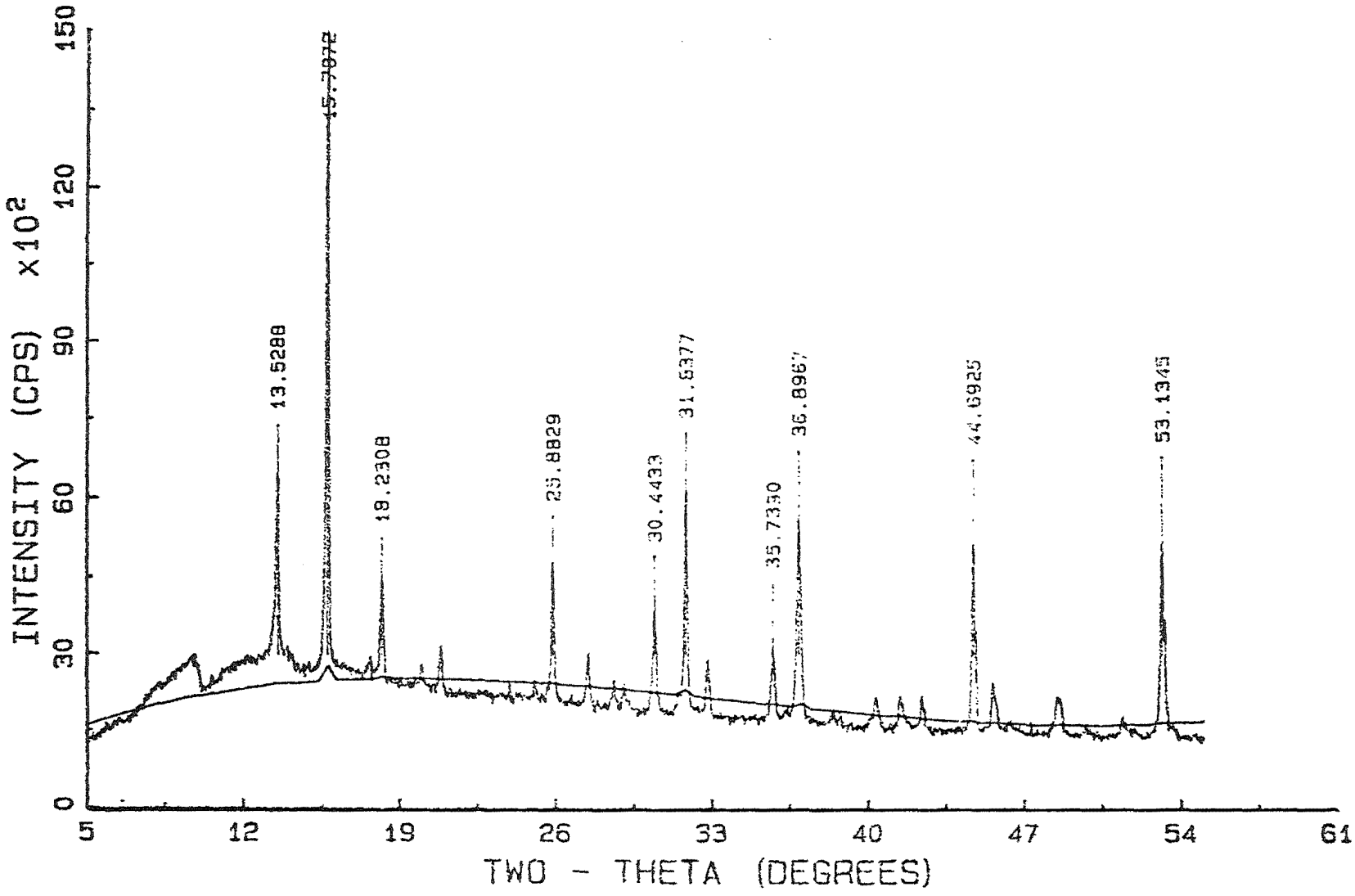


FIGURE 9.4

X-ray powder diffraction pattern of $K_3[RuCl_6]$

size or the radius ratio for the complexes studied here. The metallic radii of the three metals is quite similar (Ru 1.34 A, Rh 1.34 A and Ir 1.36 A) as are the cationic radii (K^+ 1.33 A, NH_4^+ 1.39 A) and so it is surprising that they should crystallise with different structures.

9.2.2 The ^{35}Cl NQR Spectrum of Potassium Hexachloroiridate(III)

The redetermination of the structure of $K_3[IrCl_6]$ allows for a reinterpretation of the reported NQR spectrum of the complex [Cresswell et al. 1972]. The NQR spectrum of $K_3[IrCl_6]$ consists of four resonances at room temperature and five resonances at low temperature (Table 9.1).

Temperature (K)	^{35}Cl NQR Frequencies (MHz)*
298	16.639, 17.690, 17.845, 18.435
222	17.378, 17.508, 17.753, 17.890, 18.527

TABLE 9.1

^{35}Cl NQR Frequencies for $K_3[IrCl_6]$.

* Reference Cresswell et al. (1972).

The structure of $K_3[IrCl_6]$ has one short iridium to chlorine bond [Ir(2)-Cl(3)] and the cation environment around each chlorine atom is different, particularly for Cl(1) and Cl(2) (see Chapter 10). Therefore it is possible to predict a four line NQR spectrum arising from resonances for Cl(1), Cl(2), Cl(3), and Cl's (4 to 6), with perhaps the lowest resonance arising from Cl(3). The spectrum has five lines at lower temperature and the low resonance line disappears. The five lines are still consistent with the low symmetry of the anion. There was no evidence for a change in the unit cell when the temperature was lowered (Chapter 10), but this does not necessarily mean that the molecular structure has not changed.

9.3 THE FORMATION OF TRICHLOROSTANNATO- COMPLEXES OF IRIDIUM AND RHODIUM

9.3.1 The Preparation of Trichlorostannato- Complexes of Iridium(III) and Rhodium(III)

Many preparative attempts were necessary before the complexes $K_3[IrCl_5(SnCl_3)]$, $(NH_4)_3[IrCl_5(SnCl_3)]$, $Cs_3[RhCl_3(SnCl_3)_3]$, and $Rb_3[RhCl_4(SnCl_3)_2]$ were isolated. Platinum metal complexes, including those of rhodium and iridium, containing trichlorostannato- ligands are known [Young 1968; Nelson et al. 1980; Parish 1972; Porta et al. 1967; Shapley & Osborn 1973; Taylor et al. 1966; Furlani et al. 1965; Kretschmer & Pregosin 1982; Kretschmer et al. 1983a; Kretschmer et al. 1983b; Yurchenko et al. 1976]. The objective of the present work was to produce iridium(III) complexes of the form $A_3[IrX_4(SnX_3)_2]$ for structural studies.

The rhodium complex $Cs_3[RhCl_4(SnCl_3)_2]$ and some tetraalkylammonium salts of rhodium and iridium have been reported previously [Antonov et al. 1979; Antonnov et al. 1980; Antonov et al. 1981; Elizarova et al. 1974; Kimura 1979; Kimura et al. 1976; Moriyama et al. 1984]. The method of Antonov et al. (1979) was followed but oxidation of the Ir(III) was frequently a problem. The method consisted of treating solutions of either $[IrX_6]^{2-}$ or $[IrX_6]^{3-}$ with $Sn(II)X_2 \cdot 2H_2O$ under acid conditions, and then adding the relevant cation. An iridium bromo- complex with tribromostannato- ligands could not be isolated, and Antonov et al. (1979) report that rhodium tribromostannato- complexes are often contaminated with $A_3[RhBr_6]$ complexes. Because of this, work was centred on the chloro- complexes since the hexachloro- complexes are more soluble than the bromo- analogues and contamination is less likely. Intially the reactions were carried out in the open in air using reagent grade acid, but these conditions resulted in oxidation of the iridium. Even when using purified acids and an inert atmosphere (O_2 free N_2) for the intial reaction and allowing the crystallisation to occur in a desiccator in air oxidation still occurred. Hence oxidation probably occurred during crystallisation.

Chloro- complexes containing trichlorstannato- ligands were eventually obtained as K^+ and NH_4^+ salts by allowing hot concentrated solutions as described above to cool to room temperature and evaporate to near dryness overnight i.e. reasonably rapidly. For the ammonium salt a reducing agent ($K_2C_2O_4$) was added to prevent oxidation. The rate of the crystallisation is probably an important factor in obtaining iridium(III) complexes before oxidation occurs.

The infrared spectra of $(NH_4)_3[IrCl_6]$ and $(NH_4)[IrCl_5(SnCl_3)]$ are shown in Figures 9.5 and 9.6. A new absorbance occurs in the trichlorostannato- complex at 340 cm^{-1} and a similar absorbance at 345 cm^{-1} was seen in the infrared spectrum for $K_3[IrCl_5(SnCl_3)]$ (Figure 9.7(c)) and is assigned to the ν(SnCl) stretching frequency.

The UV-visible spectrum showed no evidence for iridium(IV) and was different to that of the iridium(III) hexahalides. Study of the complexes by X-ray fluoresence established that they contained tin and iridium. The single crystal X-ray structure was determined for the K^+ salt and the complex found to be $K_3[IrCl_5(SnCl_3)]$. The ammonium salt was found to be isostructural with the potassium salt (see Chapter 10).

In addition the rubidium and caesium salts of rhodium were prepared and low frequency absorbances observed in their infrared spectra, similar to those seen for the iridium complexes (Figure 9.7). The position of this absorbance is similar to that reported by Antonov et al. (1979). X-ray fluoresence spectra of the rhodium complexes also indicated that tin was present. Elemental analytical data for the complexes suggest the stoichiometries; $Cs_3[RhCl_3(SnCl_3)_3]$ and $Rb_3[RhCl_4(SnCl_3)_2]$ (Table 9.2). Despite numerous attempts at recrystallisation, crystals of the rubidium and caesium salts of the rhodium complex were severly twinned and no data collection was carried out.

Crystalline material isolated during attempts to prepare ruthenium and iridium bromo- complexes showed no evidence for an extra absorbance in the infrared spectrum. An absorbance for ν(SnBr) may be obscured by the strong absorbance due to ν(MBr) which also occurs in this region. Antonov et al. (1979) report the frequency of ν(SnBr)

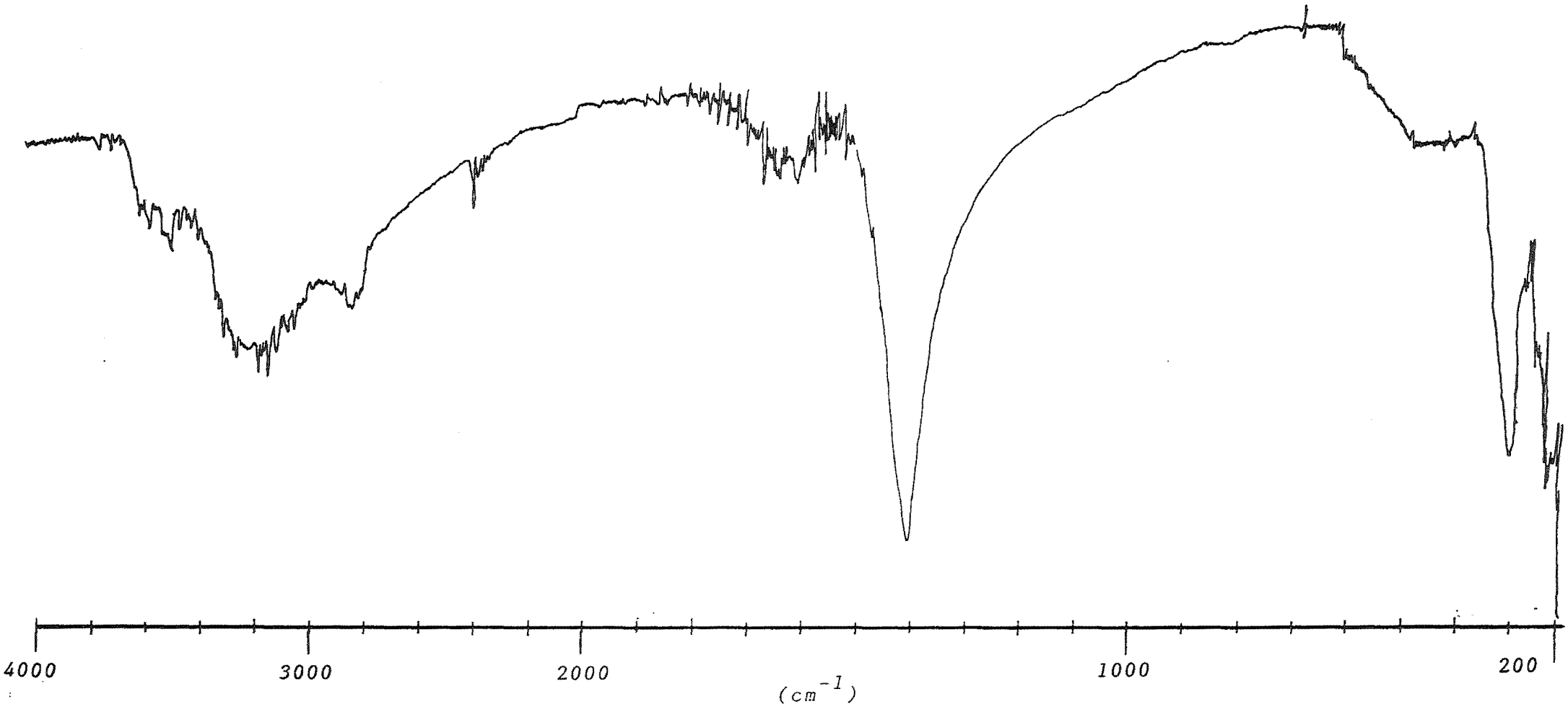


FIGURE 9.5

Infrared spectrum of $(NH_4)_3[IrCl_6]$

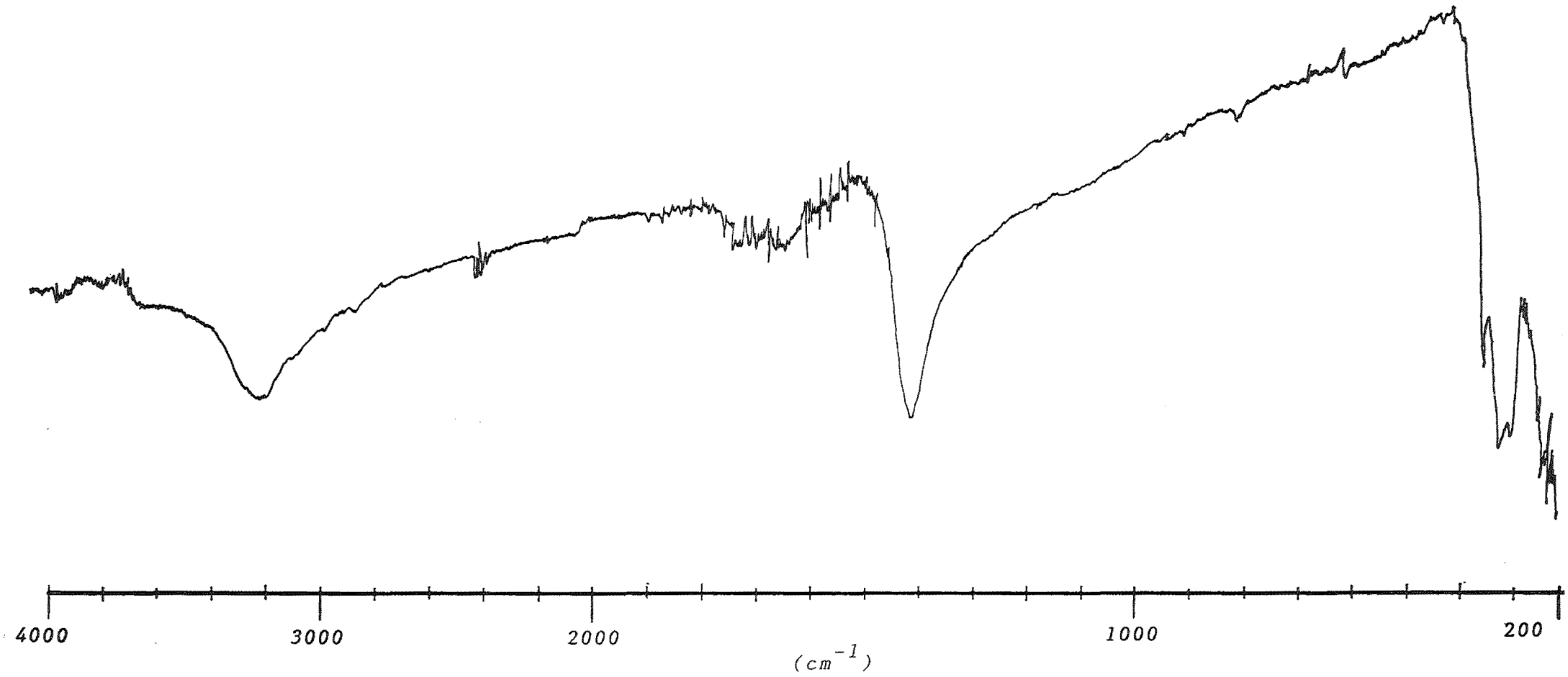
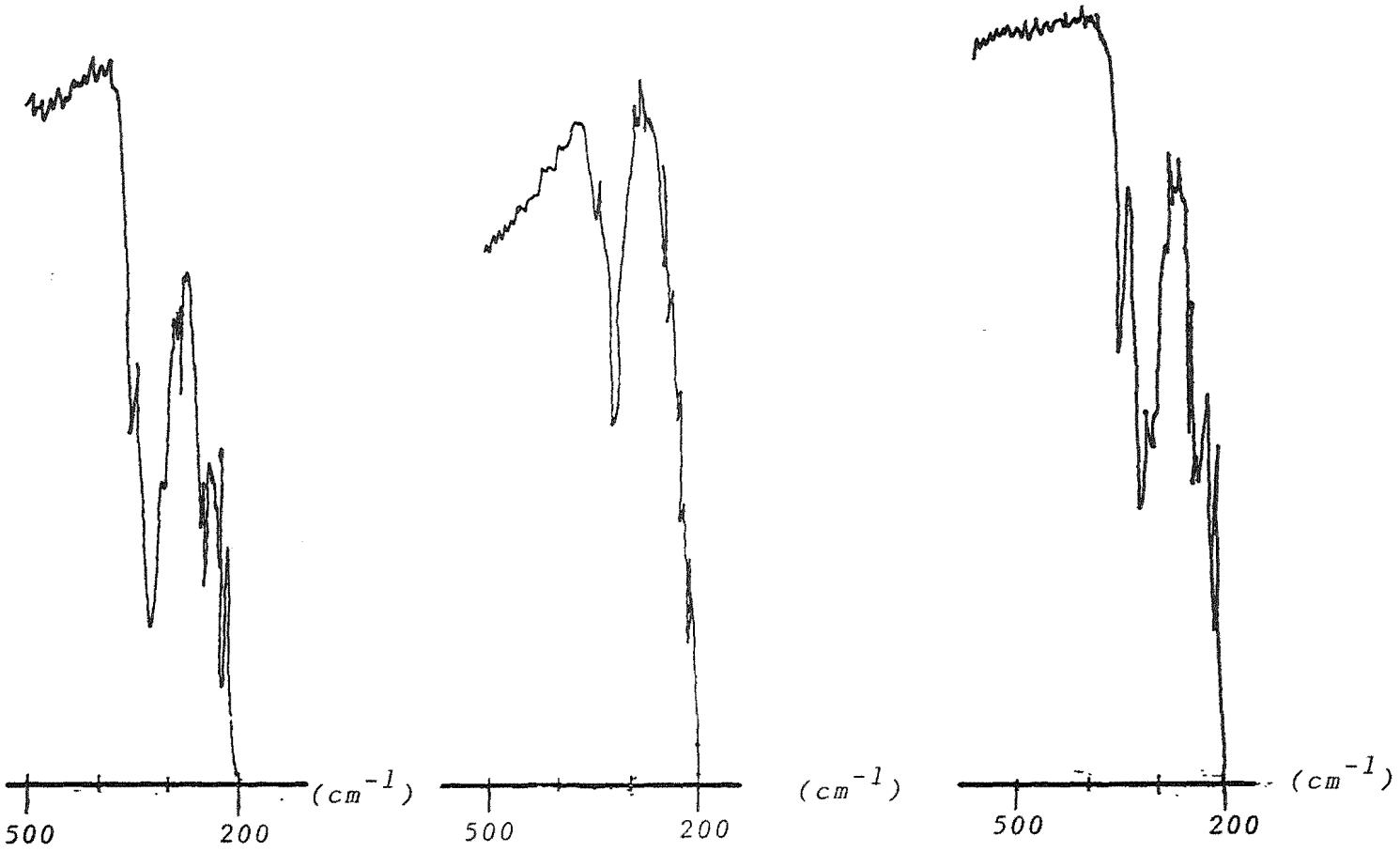


FIGURE 9.6

Infrared spectrum of $(NH_4)_3[IrCl_5(SnCl_3)]$



(A) $Rb_3[RhCl_4(SnCl_3)_2]$ (B) $Cs_3[RhCl_3(SnCl_3)_3]$ (C) $K_3]IrCl_5(SnCl_3)]$

FIGURE 9.7

Infrared spectra for platinum metal complexes with trichlorostannato- ligands.

for $(NMe_4)_3[IrBr_4(SnBr_3)_2]$ and $(NMe_4)_3[IrBr(SnCl_3)_5]$ as occurring at 215 cm^{-1}. However, the UV-visible spectra showed evidence for oxidation in all cases. Precession photography showed that the complexes belonged to the cubic crystal system and they are probably of the type $A_2[MX_6]$. Oxidation occurred readily, particularly for the iridium bromo- complexes, leading to the isolation of the complexes $(NH_4)_2[IrBr_6]$ and $(H_3O)_2[IrBr_6]$. The single crystal X-ray structures were determined for these complexes (see Chapter 10) and both complexes were found to belong to the cubic crystal system with space group Fm3m and the hexachloroplatinate $K_2[PtCl_6]$ structure.

9.3.2 Reaction Chemistry

In order to understand the reaction chemistry, a more detailed study was made of the reaction conditions used during the formation of the complex $(H_3O)_2[IrBr_6]$. The facile redox chemistry of Ir(III)/Ir(IV) halogeno- species leads to the isolation of the iridium(IV) compounds [Coll et al. 1987c]. The salt $(NH_4)_3[IrBr_6]$ was prepared in situ by adding ammonium bromide to the oxonium complex $(H_3O)_3[IrBr_6]$ in HBr obtained using a protonated ion-exchange column. The solution was then treated with $SnBr_2$ in order to obtain an Ir(III)/Sn(II) bromo- complex. It appears that even in the presence of the reducing agent $Sn(II)Br_2$ some oxidation to Ir(IV) occurred, from which the iridium(IV) oxonium salt $(H_3O)_2[IrBr_6]$ was obtained. The oxonium salt dissolved in water or 2M HBr to give a blue/purple solution, which had a UV-visible spectrum typical of $[IrBr_6]^{2-}$ (Figure 9.8) [Jorgensen 1962; Barron et al. 1982; Henning et al. 1968]. A 0.001M solution of the complex in water had a pH of 2.6, whereas the

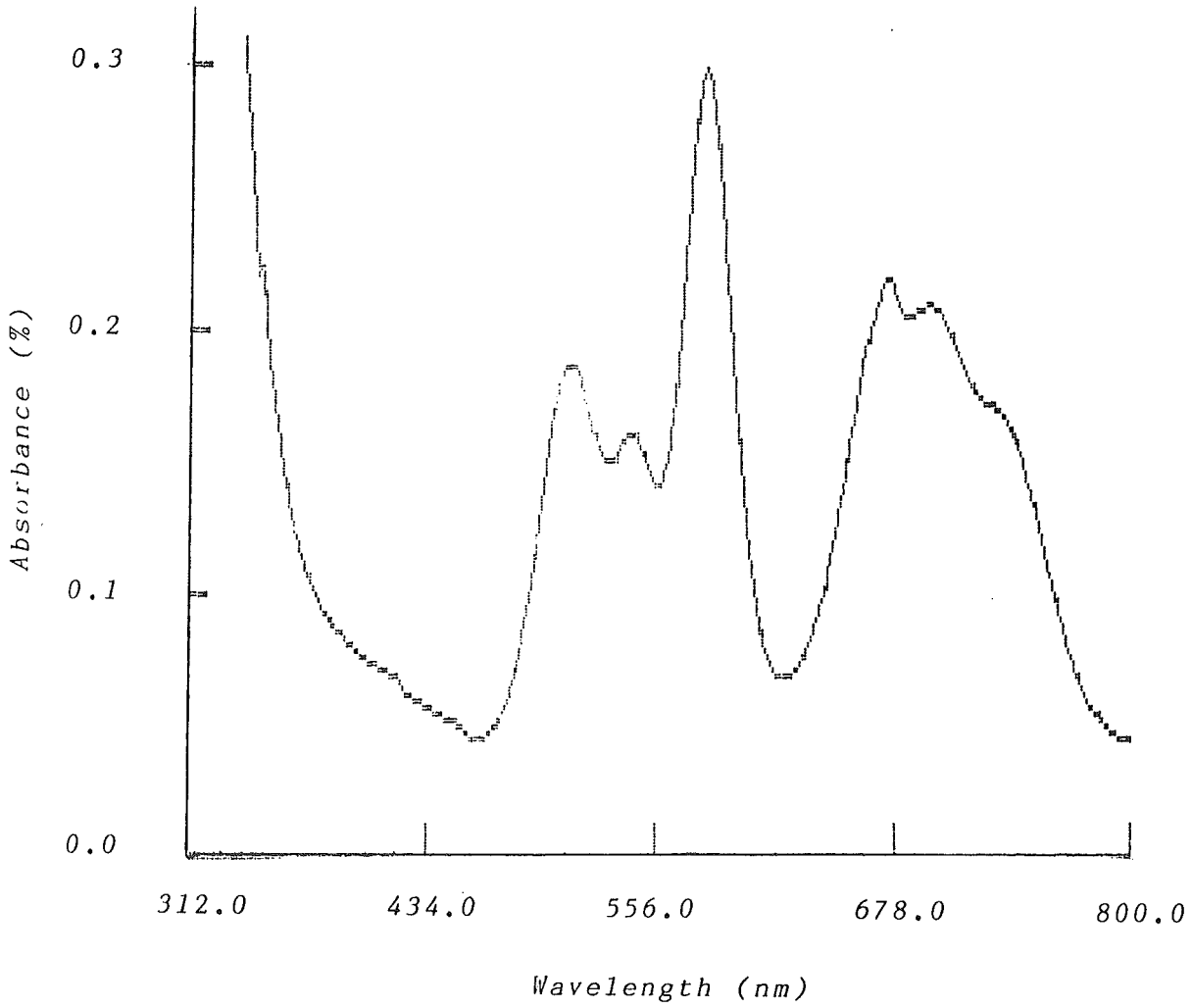
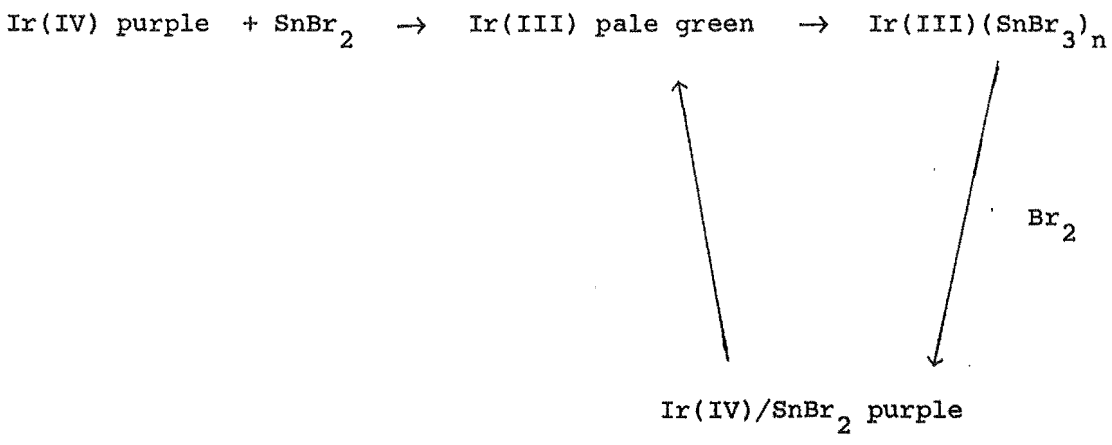


FIGURE 9.8

UV-visible spectrum of $[IrBr_6]^{2-}$

pH of a solution of $K_2[IrBr_6]$ under the same conditions was 4.9 and that of the ammonium salt 2.7. Under the microscope the crystals appeared homogenous, however, the infrared spectrum suggested there was a mixture of oxonium and ammonium salts.

A blue/purple solution of $K_2[IrBr_6]$ in reagent grade 2M HBr turned pale green on the addition of 2.5 mols of $SnBr_2$, at room temperature. Within minutes the solution had changed back to blue/purple with the same UV-visible spectrum as the starting material, except for a reduction in intensity (39 %). Addition of more $SnBr_2$ (2.5 mols) produced the pale green solution again, and this also changed back to the blue/purple solution within a few minutes. The solution spontaneously turned green again, and remained that way. The green solution had a UV-visible spectrum similar to that of Ir(III) halogeno- complexes. The colour changes observed and the interpretation is given in Scheme 9.1.



SCHEME 9.1

Redox Reaction Scheme for $Ir/SnBr_2$ system.

A repetition of the reaction using HBr purified from Br_2 gave the pale green solution on the first addition of the tin(II)bromide without any further changes. The oxidation of Ir(III) to Ir(IV) was unexpected in view of the presence of the Sn(II), and it appears that Br_2 in the HBr achieves the oxidation. Exposure of the reaction to air produces Br_2 from HBr and may explain the oxidation of the iridium as further dibromine may form from the oxidation of Br^- in air.

A number of redox reactions with favourable electrode potentials are possible, e.g.

$$2[IrBr_6]^{2-} + Sn^{2+} \rightarrow 2[IrBr_6]^{3-} + Sn^{4+}, \quad +0.87V$$

$$2[IrBr_6]^{3-} + Br_2 \rightarrow 2[IrBr_6]^{2-} + 2Br^-, \quad +0.05V$$

$$4[IrBr_6]^{2-} + 4H^+ + O_2 \rightarrow 4[IrBr_6]^{2-} + 2H_2O, \quad +0.21V$$

$$Sn^{2+} + Br_2 \rightarrow Sn^{4+} + 2Br^-, \quad +0.92V$$

$$4Br^- + 4H^+ + O_2 \rightarrow 2Br_2 + 2H_2O, \quad +0.16V$$

Some of these reactions may explain the oxidation of the original Ir(III) bromo- complex. The fact that oxidation occurred readily when reagent grade HBr was used but not when pure HBr was used suggests that the likely oxidising agent is Br_2. In view of these redox potentials it is not surprising that the Ir(IV) hexabromo- complex was

produced. Also the Ir(IV) complexes are in general less soluble than the Ir(III) complexes and thus may crystallise out more readily.

An E_h - pH diagram for the system is shown in Figure 9.9 and it is clear that dioxygen will bring about the oxidation of all species under the conditions employed i.e. at low pH, ca. 3.00 and less. The E_o value for the Sn^{4+}/Sn^{2+} system is low at +0.15 V. The UV-visible spectrum of reagent grade HBr showed a strong absorbance at 264.4 nm and this was identical to that of pure HBr to which some Br_2 was added. The Br_2 forms a complex ion Br_3^- with Br^- [Popov & Swensen 1955]. Pure HBr when treated with O_2 gives rise to some Br_2. This oxidation still occurred when some $SnBr_2$ was present confirming the predictions of the E_h - pH diagram. Kukushkin & Soboleva (1970) have reported that $K_3[IrCl_6]$ is readily oxidised by dioxgen.

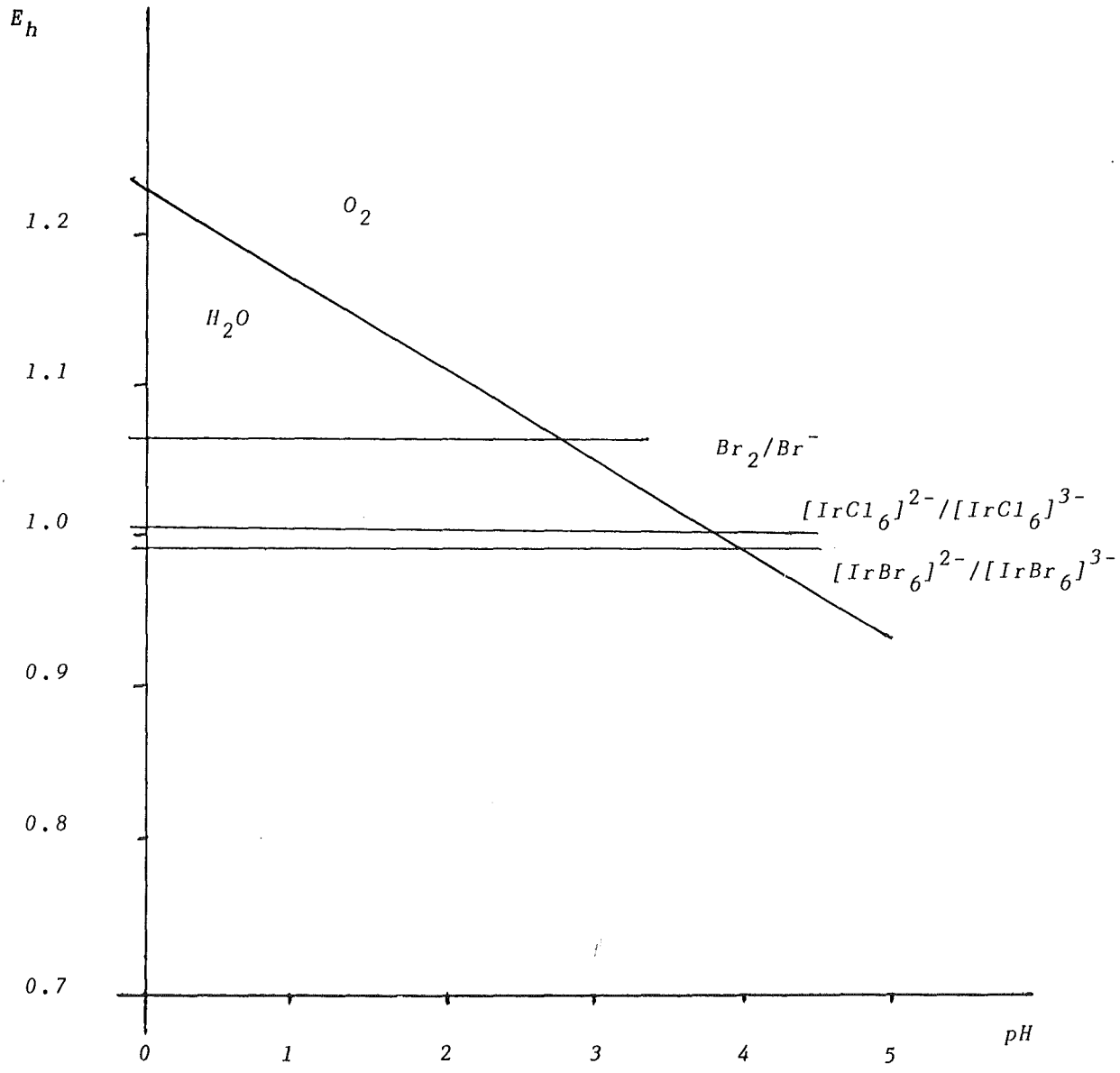


FIGURE 9.9

E_h - pH diagram for iridium/tin/bromo- system

9.4 EXPERIMENTAL

9.4.1 Preparation of the Reagents

a) Tin(II)chloride dihydrate $SnCl_2 \cdot 2H_2O$

Tin(II) chloride was obtained commercially [Hopkins] and used without furthur purification.

b) Tin(II)bromide $SnBr_2$

Tin(II) bromide was availble from previous studies in the department and may be prepared by treating tin metal with concentrated HBr [Baudler 1963].

c) Trichlororhodium(III) trihydrate $RhCl_3 \cdot 3H_2O$

The complex $RhCl_3 \cdot 3H_2O$ was obtained commercially [Alfa] and used without furthur purification.

d) Hydrogen chloride

Hydrogen chloride was prepared by the addition of concentrated sulphuric acid onto a solution of concentrated HCl [Dodd & Robinson 1954]

e) Pure hydrobromic acid

Reagent grade HBr was purified by standing over red phosphorus for 24 hours and then distilling. Pure hydrobromic acid is colourless

and boils at 126 ^{o}C. When stored in a dark bottle there was no evidence of discolouration after three months.

9.4.2 Preparation of the Complexes

a) Potassium hexachloroiridate(IV) $K_2[IrCl_6]$

The complex $K_2[IrCl_6]$ was prepared as described by Rankin (1978) by mixing iridium metal powder (2.0g) intimately with the stoichiometric quantity of potassium chloride (2.33g) in a silica boat and heating in a tube furnace at 600 ^{o}C in a stream of Cl_2 gas for a minimum of one hour. The dark solid obtained was extracted with hot 4M HCl (two 70ml portions) and the volume reduced under vacuum to produce tiny octaherdal shaped dark red crystals. Potassium hexachloroiridate(IV) dissolves in water to form a intense dark red solution with a UV-visible spectrum characteristic of iridium(IV) [Jorgensen 1962]

b) Sodium hexahalogenoiridates(IV) $Na_2[IrX_6]$

The complexes $Na_2[IrCl_6]$ and $Na_2[IrBr_6]$ were prepared as outlined in Chapter 5.

c) Potassium hexabromoiridate(IV)

$K_2[IrBr_6]$

Potassium hexachloroiridate(IV) was dissolved in the minimum of pure concentrated HBr and evaporated to dryness carefully on a steam

bath. The process was repeated twice to ensure completion of the exchange.

d) Oxonium hexabromoiridate(IV) $(H_3O)_2[IrBr_6]$

Potassium hexabromoiridate(III) (0.2g) dissolved in double distilled water (50ml) was slowly passed down a protonated cation exchange column (Dowex 50W-X8). The stoichiometric amount of ammonium bromide (0.05g) dissolved in 2M hydrobromic acid (5ml) was added to the effluent. The volume of the solution was reduced to near dryness by heating, and the residue taken up in hot reagent grade concentrated hydrobromic acid. To this solution was added the stoichiometric (2.5x) amount of $SnBr_2$ (0.19g) dissolved in concentrated hydrobromic acid (10ml). The solution was left in a desiccator over potassium hydroxide pellets. After several weeks small dark octahedral shaped crystals appeared (0.03g) and were collected and washed with acetone and diethylether and air dried. The crystals were found from a single crystal X-ray analysis to be oxonium hexabromoiridate(IV) $(H_3O)_2[IrBr_6]$.

e) Potassium and ammonium hexachloroiridate(III) hydrate

$A_3[IrCl_6].H_2O$ for A = K, NH_4

These complexes may be prepared by treating a solution of the iridium(IV) complex with a reducing agent [Kukushikin & Soboleva 1970; Rankin 1978]. The K^+ salt was prepared using potassium oxalate as the reducing agent. The complex $K_2[IrCl_6]$ (0.5g) was dissolved in double distilled water with heating and the stoichiometric quantity of $K_2C_2O_4$ (0.09g) added. The dark colour of the solution faded as the soution

was heated and there was evidence for the evolution of a gas (CO_2). After ten minutes of heating the solution was a yellow/green colour and an excess of the oxalate (0.09g) was added to ensure complete reduction. The solution was carefully evaporated to dryness on a water bath and the pale green residue taken up in the minimum amount of hot 2M HCl and placed in a desiccator over potassium hydroxide pellets. After 5 - 7 days large pale green block shaped crystals of $K_3[IrCl_6].H_2O$ were formed.

The ammonium complex was similarly prepared using $(NH_4)_2[IrCl_6]$ as the starting material.

f) Potassium and ammonium hexachloroiridate(III)

$A_3[IrCl_6]$ for A = K, NH_4

The hydrated salt prepared in (e) was taken up in the minimum amount of 12M HCl saturated with HCl gas and allowed to crystallise out over potassium hydroxide pellets in a desiccator. After 2 - 3 weeks pale green diamond shaped thin plate crystals appeared. The structure of the K^+ salt was determined by single crystal X-ray diffraction, and the NH_4^+ salt by X-ray powder diffraction and precession photography. Both complexes had UV-visible spectra typical of Ir(III) [Jorgensen 1962] and showed no absorbance for H_2O in their infrared spectra.

g) Potassium and ammonium pentachloro(trichlorostannato)-iridate(III) $A_3[IrCl_5(SnCl_3)]$ for A = K, NH_4

A procedure similar to that used to prepare the rhodium complex $Cs_3[RhCl_4(SnCl_3)_2]$ was used [Antonov et al. 1979]. The complex

$(NH_4)_3[IrCl_6]$ (0.13g) was dissolved in reagent grade concentrated HCl (10ml) and $SnCl_2.2H_2O$ (0.12g) dissolved in reagent grade concentrated HCl (10ml) and heated for ten minutes on a water bath. The pale green solution initially became more pale and then as the solvent was evaporated became darker. Potassium oxalate (0.04g) was added and the solution heated for a further ten minutes. The solvent volume was reduced to 10 - 12 ml and the hot solution allowed to cool to room temperature. The solution was left in an open beaker and overnight evaporated to near dryness. Small thin plate irregularly shaped dichroic red-green crystals were obtained. The infrared spectrum showed an absorbance at 340 cm^{-1} assigned to ν(Sn-Cl) and the compex was found to isostructural with the K^+ salt (Chapter 10).

The potassium salt was prepared similarly but no oxalate was used. The potassium salt also formed dichroic red-green thin plate crystals and showed an absorbance in the infrared spectrum at 345 cm^{-1} assigned to ν(Sn-Cl). The complex was characterised by single crystal X-ray diffraction (Chapter 10).

h) Potassium hexachlororhodate(III) hydrate

$K_3[RhCl_6].H_2O$

The complex $K_3[RhCl_6].H_2O$ was prepared as described by Fergusson & Sherlock (1977). The complex $RhCl_3.3H_2O$ (1.0g) was dissolved in 3M HCl (20ml) and potassium chloride (0.86g) dissolved in 3M HCl (10ml) added. The solution was heated on a water bath for 30 minutes and the solvent volume reduced. The solution was placed in a desiccator over potassium hydroxide pellets and after a few days red crystals of $K_3[RhCl_6].H_2O$ appeared. The crystals were collected, washed with cold

ethanol and diethylether, and air dried. The unit cell parameters for the complex were determined on the X-ray diffractometer and found to agree with previously reported values [Cresswell et al. 1972].

i) Potassium hexachlororhodate(III)

$K_3[RhCl_6]$

Potassium hexachlororhodate(III)hydrate as made in (h) was placed in a oven at 150 ^{o}C and left overnight. Attempts to prepare this complex by recrystallising $K_3[RhCl_6].H_2O$ from concentrated HCl were unsuccessful and only the hydrate was obtained. The salt had an UV-visible spectra characteristic of Rh(III) [Jorgensen 1962], and the infrared spectrum showed no evidence for H_2O.

j) Salts of tetrachlorobis(trichlorostannato)rhodate(III) and trichlorotris(trichlorostannato)rhodate(III)

The complexes $Cs_3[RhCl_3(SnCl_3)]$ and $Rb_3[RhCl_4(SnCl_3)_2]$ were prepared in a similar way to that used for the iridium complexes but using $RhCl_3.3H_2O$ as the starting material. No oxalate was used. The presence of tin in all complexes was confirmed by X-ray fluoresence spectroscopy and the infrared spectra showed new absorbances assignable to ν(SnCl) (Figure 9.7). The elemental analytical results confirmed the above stoichiometry (Table 9.2)

k) Potassium hexachlororuthenate(III)

$K_3[RuCl_6]$

The complex $K_3[RuCl_6]$ was prepared by the method of James and McMillan (1975). Hydrated trichlororuthenium(III) $RuCl_3 \cdot 3H_2O$ (1.0g) in methanol (50ml) was heated under reflux in an atmosphere of H_2 for five hours. The yellow-brown solution became dark green after this time, KCl (0.9g) was added and the solution heated under reflux in air until the KCl dissolved. A brown precipitate formed which was collected, washed with methanol and recrystallised from 12M HCl. The crystalline material was found to have a UV-visible spectrum identical to that reported for $[RuCl_6]^{3-}$ [Jorgensen 1962], and an infrared spectrum similar to that of $K_3[IrCl_6]$.

Compound	Infrared cm^{-1}	Elemental Anal. %Cl Found(Calc.)
$K_3[IrCl_5(SnCl_3)]$*	345	
$(NH_4)_3[IrCl_5(SnCl_3)]$*	340	
$Rb_3[RhCl_4(SnCl_3)_2]$	340	33.2(33.2)
$Cs_3[RhCl_3(SnCl_3)_3]$	340	37.2(37.3)

TABLE 9.2

Summary of elemental analytical results, and spectroscopic data.

* structure determined by single crystal X-ray diffraction.

CHAPTER 10

THE STRUCTURAL CHEMISTRY OF SOME PLATINUM METAL HALOGENO-COMPLEXES

10.1 INTRODUCTION

In this chapter the crystal structures of four new complexes are described. The complexes studied were; $K_3[IrCl_6]$, $(H_3O)_2[IrBr_6]$, $(NH_4)_2[IrBr_6]$, and $K_3[IrCl_5(SnCl_3)]$. The structures were solved using data collected at low temperature. The heavy atom positions were deduced from the Patterson map and the structures solved using the heavy atom method. All structures were corrected for the effects of absorption and anisotropic thermal parameters were used for the heavy atoms. The general techniques used are described in Chapter 11 and the specific details in this chapter.

10.2 THE CRYSTAL AND MOLECULAR STRUCTURE OF POTASSIUM HEXACHLOROIRIDATE(III) $K_3[IrCl_6]$

10.2.1 Introduction

This structural determination is a repeat of a previous analysis carried out in the department [Rankin et al. 1983; Rankin 1978]. Comments by a referee indicated that the original structure solution was based on the wrong space group and it turned out that it was necessary to redetermine the structure. The original analysis found the crystal system to be triclinic and the space group $P\bar{1}$. However,

the present analysis found the crystal system to be monoclinic and the space group $P2_1/c$.

10.2.2 Data Collection

A small thin plate crystal was placed on the diffractometer in a random orientation, and centred. Rotation photographs were necessary to locate reflections and these were centred and used to calculate possible unit cells. The best cell determined was a primitive monoclinic cell and the data collection was carried out on this basis. Refined unit cell parameters were determined by the least squares refinement of 25 accurately centred reflections ($29 < 2\theta < 31$). In the data collection the intensities of 1824 unique reflections were measured using the ω-scan technique ($3 < 2\theta < 55$) and variable scan rate ($4.88 - 29.3\ ^{\circ}min^{-1}$). Of these 1287 were found to have an intensity greater than 3σ and were used in the structure solution and refinement. Mosaicity was checked before the data collection by inspection of peak profiles of several strong low angle reflections in different directions through the crystal. The peaks were symmetrical and their width at half height was found to be less than 0.3° which is acceptable.

Crystal stability was monitored for movement or crystal deterioration, by recording three standard reflections every 100 reflections. No significant variation was observed and the reflections had an intensity of within 5% of the starting values at the end of the data collection.

The experimental parameters and crystal data are summarised in Tables 10.1 and 10.2.

Formula	$K_3[IrCl_6]$
Formula weight	522.22
Crystal system	monoclinic
Space group	$P2_1/c$
a	12.500(7) Å
b	7.424(6) Å
c	11.831(10) Å
α	90.00(0)°
β	108.48(6)°
γ	90.00(0)°
Volume	1041.4 (14) $Å^3$
F(000)	943.81
μ	162.22 cm^{-1}

TABLE 10.1

Crystal data for $K_3[IrCl_6]$

Temperature	123 K
Radiation	Mo $K\alpha$ (0.71069a)
Scan range	2.4^{o}
Bragg angle range	$5 - 55^{o}$
Scan speed	variable ($4.88 - 29.3\ ^{o}min^{-1}$)
Crystal dimensions	0.26mm x 0.34mm x 0.08mm
Crystal volume	$0.0071\ mm^{3}$
Calculated density	$3.33\ g\ cm^{-3}$
Measured density	$> 3.31\ g\ cm^{-3}$
Molecules per unit cell	four
Mosaicity	$< 0.3^{o}$
Unique reflections	1824
Reflections used in refinement	1287
Ratio observations to variables	1287:95 (13.5:1)
Range of transmission factors	0.01219 - 0.18778

TABLE 10.2

Data collection parameters for $K_3[IrCl_6]$

10.2.3 Structure Solution and Refinement

The data was treated for polarisation and Lorentz effects, and the structure solution attempted using the direct methods. This was unsuccessful resulting in an electron density map that was very fragmented and which did not make chemical sense. Consequently the Patterson map was obtained from which the iridium atoms were located and Fourier difference maps used to locate the chlorine and potassium atoms.

Corrections were intially applied for absorption using an empirical model based on ψ-scans but this method did not significantly improve the refinement, and a Gaussian face indexing procedure was used and proved to be much more successful. The amount of absorption was considerable as suggested by the high value for the linear absorption coefficient (μ = 162.22 cm^{-1}) and the application of this correction resulted in a dramatic improvement in the refinement of the structure. The value of R fell from 0.2317 to 0.1234 upon the application of this correction. The difference between the maximum and minimum absorbance is very large as is the actual absorbance. This is due to the large value of the linear absorption coefficient and because the crystal was a thin plate, there is a large difference in the path length of the diffracted X-ray beams as they pass through the crystal in different directions.

All atoms were assigned anisotropic thermal parameters. This resulted in an improvment in R from 0.1234 to 0.0703. The best fit of observed to calculated data was achieved by using a weighted least squares procedure, initially using a fixed weighting scheme, and at

the final stages of the refinement allowing the weighting to vary. This led to an improvement in R to a value of 0.0694.

Inspection of the difference between the observed and calculated structure factors for strong low angle reflections indicated secondary extinction was occurring. Correction for the effects of secondary extinction improved R to a final value of 0.0677 and a goodness of fit of 2.031.

10.2.4 Description of the Structure

The atom positions and anisotropic temperature factors are given in Tables 10.3, and 10.4. The structure of the asymmetric unit is given in Figure 10.1(A). In Figure 10.1(B) the symmetry related chlorine atoms have been drawn to illustrate more clearly the different orientation of the two anions. The packing within the unit cell is illustrated in Figure 10.2.

The coordination of the anions is simple with the chlorine atoms bonded in an octahedral arrangement to the iridium atoms. The iridium atoms are located at 0, 0, 0 and 0.5, 0, 0.5, which are special positions for the space group $P2_1/c$ and are centres of inversion. The asymmetric unit consists of two different half molecules; one centred at the origin and the other at 0.5, 0, 0.5. The total of four molecules per unit cell are generated from the asymmetric unit by the symmetry requirements of the space group.

10.2.5 Discussion

The iridium to chlorine bond lengths are in the range 2.352(4) - 2.373(4) Å and are similar to those reported for other Ir(III)

Atom	X	Y	Z	U*
Ir(1)	0000	0000	0000	8(1)
Ir(2)	5000	0000	5000	8(1)
Cl(1)	6176(4)	0010(5)	3787(4)	20(2)
Cl(2)	3760(4)	1897(6)	3596(3)	23(1)
Cl(3)	4066(4)	-2596(6)	3992(4)	22(2)
Cl(4)	1405(4)	-2055(6)	1030(3)	23(2)
Cl(5)	1476(4)	1927(6)	-0058(3)	24(2)
Cl(6)	0005(4)	1307(5)	1817(3)	19(1)
K(1)	8188(4)	0660(6)	6138(3)	26(1)
K(2)	8161(4)	-0673(6)	2646(3)	26(1)
K(3)	5981(4)	4615(6)	3592(4)	31(2)

TABLE 10.3

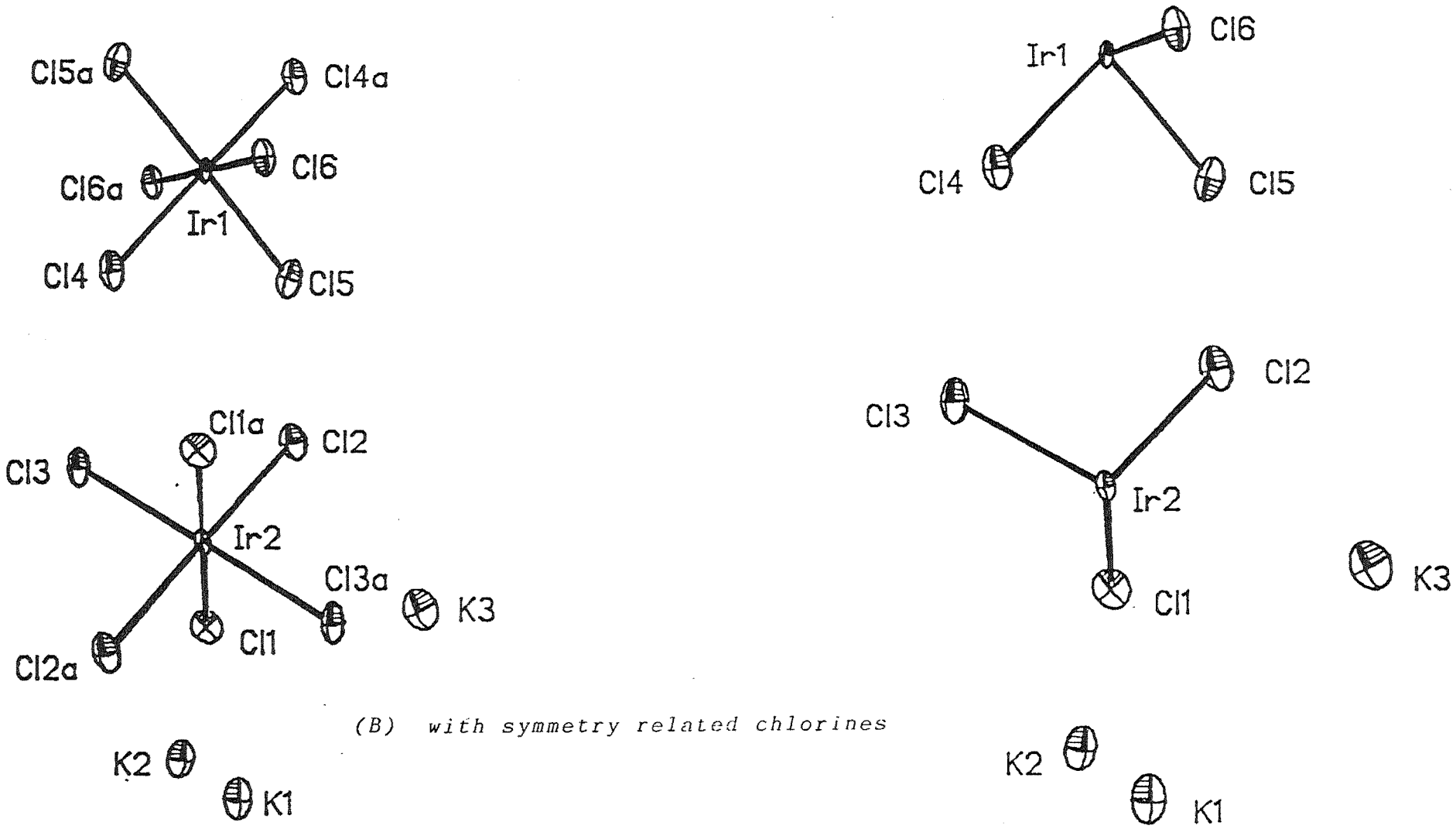
Atom coordinates ($\times 10^4$) and temperature factors ($\times 10^3$) for $K_3[IrCl_6]$.

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir(1)	15(1)	4(1)	4(1)	1(1)	3(1)	0(1)
Ir(2)	15(1)	6(1)	3(1)	1(1)	2(1)	2(1)
Cl(1)	26(3)	25(3)	10(2)	1(1)	2(1)	2(1)
Cl(2)	33(3)	18(2)	15(2)	6(2)	7(2)	5(2)
Cl(3)	36(3)	12(2)	19(2)	-4(2)	10(2)	0(2)
Cl(4)	38(3)	16(2)	12(2)	3(2)	6(2)	3(2)
Cl(5)	41(3)	18(2)	14(2)	0(2)	11(2)	-7(2)
Cl(6)	34(2)	13(2)	12(2)	-1(2)	9(2)	3(2)
K(1)	42(3)	18(2)	18(2)	-0(2)	10(2)	-1(2)
K(2)	41(3)	21(2)	17(2)	-4(2)	11(2)	-4(2)
K(3)	40(3)	32(2)	21(2)	7(2)	10(2)	6(2)

TABLE 10.4

Anisotropic temperature factors ($Å^2 \times 10^3$) for $K_3[IrCl_6]$



(B) with symmetry related chlorines

(A) asymmetric unit

FIGURE 10.1

Perspective view of the structure of $K_3[IrCl_6]$

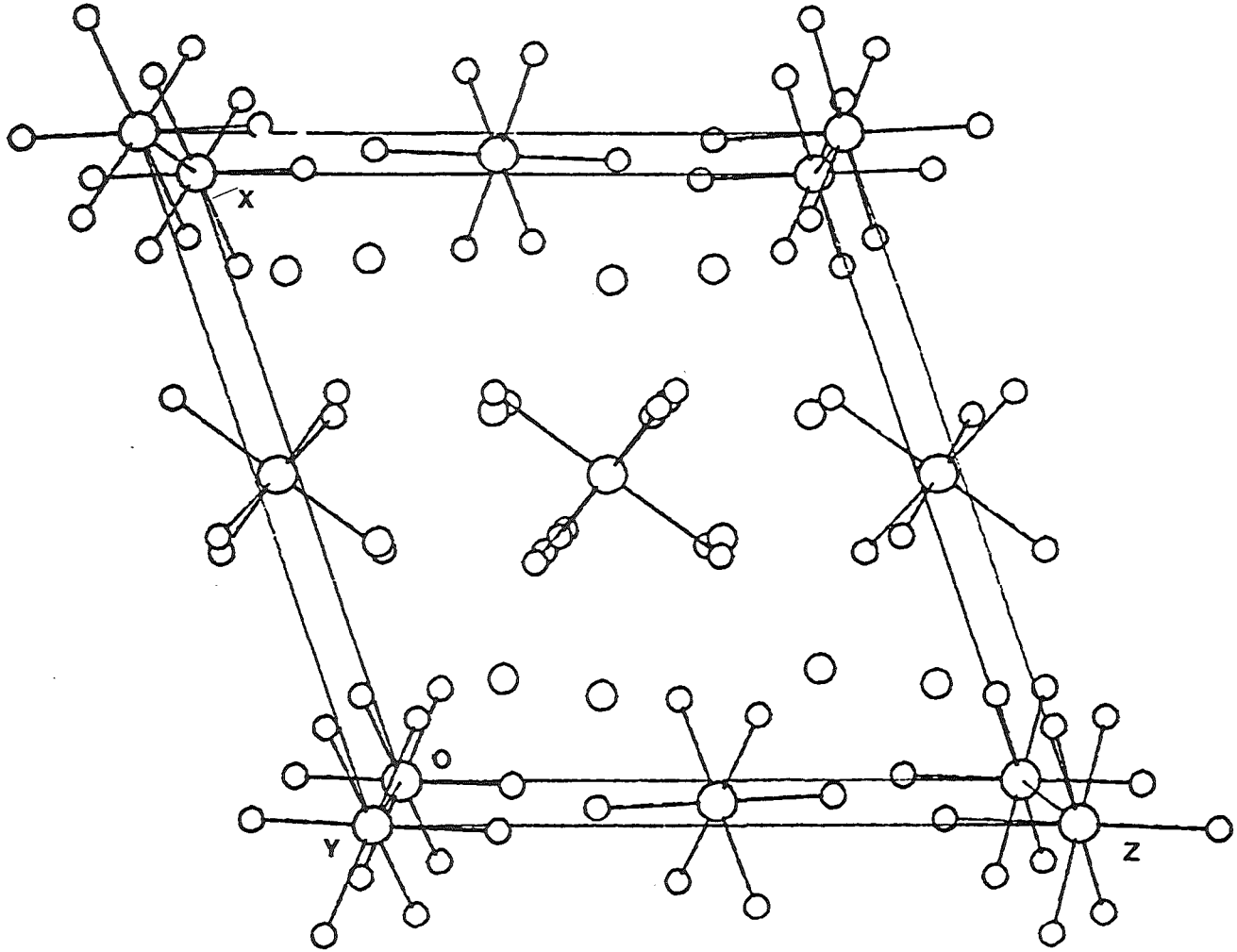


FIGURE 10.2

Unit cell packing for $K_3[IrCl_6]$

structures [Wycoff 1965; Rankin et al. 1983]. The anionic units do not have perfect octahedral coordination and there are deviations of up to 3.3^{o} from 180^{o}. One Ir-Cl bond length, that for Ir(2) and Cl(3), is slightly longer than the others; 2.373(4) Å compared with 2.352(5) - 2.357(4) Å. The bond lengths are given in Table 10.5, and the bond angles in Table 10.6. There are no close non-bonded contacts as can be seen from Table 10.7. The difference in the bond lengths and variations in angle from the perfect octahedral arrangement are likely to be due to distortions arising from the packing within the lattice.

All atoms undergo considerable anisotropic thermal vibration, and they appear to be vibrating more along one direction in the lattice rather than in different directions.

An interesting and unusual feature of this structure is the different orientation of the anions. The anion positions at the origin and at 0.5, 0, 0.5 are slightly different so that there is a partial or psuedo centring. This gives rise to the situation in which, whilst many extinctions occur, there are still some reflections present that would be absent if the two anions had the same orientation.

The overall molecular structure found from this structural determination is quite similar to the original analysis [Rankin et al. 1983] except that there is now no need to postulate disorder and there is less thermal vibration of some atoms.

The original unit cell obtained by Rankin (1978) of a = 12.631(2) Å, b = 7.029(1) Å, c = 7.027(1) Å, $\alpha = 116.12(2)^{o}$, $\beta = 91.21(9)^{o}$, $\gamma = 106.88(9)^{o}$ was transformed by Dr. G. Gainsford of the D.S.I.R. using

Bond	Length	Bond	Length
Ir(1) - Cl(4)	2.357(4)	Ir(1) - Cl(5)	2.352(5)
Ir(1) - Cl(6)	2.357(4)	Ir(2) - Cl(1)	2.353(6)
Ir(2) - Cl(2)	2.352(4)	Ir(2) - Cl(3)	2.373(4)

TABLE 10.5

Bond lengths (Å) for $K_3[IrCl_6]$

Bond	Angle	Bond	Angle
Cl(4) - Ir(1) - Cl(5)	86.8(2)	Cl(1) - Ir(2) - Cl(3)	89.9(2)
Cl(5) - Ir(1) - Cl(6)	89.9(2)	Cl(1) - Ir(2) - Cl(1a)	180.0(0)
Cl(5) - Ir(1) - Cl(4a)	93.2(2)	Cl(3) - Ir(2) - Cl(1a)	90.1(2)
Cl(6) - Ir(1) - Cl(5a)	90.1(2)	Cl(1) - Ir(2) - Cl(2)	88.1(2)
Cl(4) - Ir(1) - Cl(6a)	89.7(1)	Cl(2) - Ir(2) - Cl(3a)	88.9(2)
Cl(6) - Ir(1) - Cl(6a)	180.0(0)	Cl(2) - Ir(2) - Cl(2a)	88.9(1)

TABLE 10.6

Bond angles (deg) for $K_3[IrCl_6]$

Atoms	Distance	Atoms	Distance
K1 - Cl1	3.149	K2 - Cl5	8.186
K1 - Cl2	5.485	K2 - Cl6	10.035
K1 - Cl3	5.534	K3 - Cl1	3.430
K1 - Cl4	8.966	K3 - Cl2	3.433
K1 - Cl5	9.302	K3 - Cl3	5.943
K1 - Cl6	9.909	K3 - Cl4	7.454
K2 - Cl1	3.214	K3 - Cl5	6.255
K2 - Cl2	6.246	K3 - Cl6	7.509
K2 - Cl3	5.987	K3 - Cl1a	5.823
K2 - Cl4	8.115	K3 - Cl3a	3.246

TABLE 10.7

Selected non-bonding contacts (Å) for $K_3[IrCl_6]$

the program XCREDUC. This produced a centred monoclinc lattice with unit cell constants; a = 11.928 Å, b = 7.4361 Å, c = 12.5455 Å, and β = 108.05°. The space group was found to be C2/m. During the preliminary search for the correct unit cell, a monoclinic unit cell of similar dimensions was also obtained. However, several strong reflections were observed that were inconsistent with a centring condition existing in the lattice. Thus the data collection was based on a primitive unit cell. At the end of the data collection, examination of the systematic absences indicated that the space group was $P2_1/a$, which was changed to the more conventional setting of $P2_1/c$. The difference in the unit cell dimensions, between the unit cell measured in this structural determination and the monoclinc C-centred unit cell obtained from Gainsford's transformation of the original triclinic unit cell, are probably due to the fact that the transformed unit cell is based on unit cell parameters that were obtained from a data collection that was carried out at room temperature whereas the new data was collected at 123 K. The lower temperature would result in a slight contraction of the unit cell leading to shorter axial lengths.

Structural changes with a change in temperature have been reported for platinum metal halogeno- complexes [Griffith 1967; Armstrong & van Driel 1972; Seddon & Seddon 1984]. However, these usually involve temperatures somewhat lower than that used in this analysis [Armstrong & van Driel 1972]. To check whether a change had occurred from a triclinic unit cell at room temperature to a monoclinc unit cell at low temperature, a crystal was mounted on the diffractomer and the unit cell determined before and after lowering

the temperature. This was repeated using several crystals and there was no evidence for a structural change.

It had been stated [Rankin et al. 1983] that the ammonium salt $(NH_4)_3[IrCl_6]$ was isostructural with the potassium salt having a similar X-ray powder photograph. Rankin also studied the NH_4^+ salt using precession photography and obtained a unit cell of similar dimensions to that of the K^+ salt. It was decided to redetermine the unit cell constants of $(NH_4)_3[IrCl_6]$ on the basis of the monoclinic unit cell of the K^+ salt using precession photography. However, the results of this indicated that the unit cell for the ammonium salt was orthorhombic with dimensions 7.36 Å, 7.09 Å, 10.13 Å. Attempts to transform the monoclinic unit cell of the potassium complex into an orthorhombic unit cell were unsuccessful. The program was also unable to find a monoclinc unit cell similar to that of $K_3[IrCl_6]$ when the unit cell parameters for the orthorhombic $(NH_4)_3[IrCl_6]$ were given. Since the ammonium and potassium complexes were claimed to be isostructural, a further crystal of the potassium complex was studied and an attempt made to confine the unit cell to an orthorhombic one. This was to ensure that the potassium complex could not be orthorhombic. When the unit cell of the potassium complex was constrained to the orthorhombic crystal system, very high standard deviations for the values of the unit cell lengths and volume were observed. The error in the unit cell volume was of the order of 60 parts in 1000 as compared with 1.3 in 1400 for the monoclinc unit cell and so the lower symmetry unit cell would seem to be confirmed. In addition axial photographs were taken and these indicated that the lattice symmetry was defintely monoclinic.

The potassium and ammonium salts were thought to be isostructural [Rankin et al. 1983] because they had similar powder diffraction photographs and precession photographs. The X-ray powder diffractograms were measured for both salts and are given in Chapter 9. As can be seen they are quite different. The fact that the X-ray powder diffractograms are different, and the original triclinic unit cell for the potassium salt is definitely incorrect, suggests that the potassium and ammonium salts are neither isomorphous nor isostructural.

10.3 THE CRYSTAL AND MOLECULAR STRUCTURE OF OXONIUM HEXABROMOIRIDATE(IV) $(H_3O)_2[IrBr_6]$

10.3.1 Introduction

The structure of $(H_3O)_2[IrBr_6]$ was determined on a crystalline material that was isolated during attempts to produce a tribromostannato- complex of iridium. The cation was initially thought to be the ammonium ion, but the analysis indicated that it was the oxonium ion.

The structure was fully solved in the tetragonal crystal system space group I4mm, but later solved in the cubic crystal system space group Fm3m with the potassium hexachloroplatinate(IV) $K_2[PtCl_6]$ structure [Wycoff 1965].

10.3.2 Data Collection

Initial precession photographs indicated that the unit cell belonged to the higher symmetry Laue group 4/mmm of the tetragonal crystal system. Systematic absences were observed for h + k + l = 2n + 1 which is a body centring condition. It is not possible to determine a unique space group from these absences and there are five different possibilites; I4mm, I422, $I\bar{4}2m$, $I\bar{4}m2$ and I4/mmm. A small dark octahedral shaped crystal was placed on the diffractometer and centred. Since the unit cell was small and the symmetry high, rotation photographs were necessary to find enough reflections to confirm the unit cell. Refined cell parameters and standard deviations were obtained from the least squares refinement of 25 accurately centred reflections. The mosaicity of several reflections

was checked in different directions through the crystal. The intensities of 475 unique reflections were measured using the ω-scan technique. Of these 394 had an intensity greater than 3σ and were used in the structure solution and refinement.

Crystal stability was monitored by recording three standard reflections every 100 reflections and there was no significant variation observed.

10.3.3 Structure Solution and Refinement

The structure was solved initially in the space group I4mm. The data was treated for Lorentz and polarisation effects. The positions of the iridium atoms were deduced directly from the Patterson map. Subsequent difference maps indicated that there were no tin atoms present, only bromine and oxygen.

An empirical absorption correction based on ψ-scans was applied, and as has been observed for other crystals of iridium complexes a dramatic improvement occurred in the refinement of the structure. The minimum transmission factor was 0.521 and the maximum was 0.958. Such a large difference in the transmission factors indicates the importance of absorption in this crystal. This was reflected in the large improvement in R from 0.0727 to 0.0427.

All atoms were assigned anisotropic thermal parameters and a weighted least squares procedure, allowing the weighting parameter to vary, was used at the end of the refinement. This led to a final R of 0.0366, a weighted R of 0.0362, and a goodness of fit of 0.947.

Comparison of the observed and calculated structure factors showed no evidence of extinction.

The positional and thermal parameters of the bromine atoms were restrained by the use of free variables [Sheldrick 1984]. This involved using an instruction within the refinement that allowed the positional parameters to refine whilst restricting them to certain conditions. This was necessary since the atoms were on special postions. One of the bromine atoms was on a position of the type x, x, z the second bromine was at 0, 0, z, the oxygen at 0.5, 0, z, and the iridium at 0, 0, z. The zero coordinates of these atoms were fixed and the other coordinates allowed to refine.

There was no obvious reason why the complex did not crystallise with the potassium hexachloroplatinate $K_2[PtCl_6]$ structure as for similar complexes $K_2[OsBr_6]$, $(NH_4)_2[OsBr_6]$, $(NH_4)_2[PtBr_6]$ [Griffith 1967]. It was however observed that the two Ir-Br bond lengths were the same within experimental error and that the diagonal of the xy face of the cell was very close to the length of the z direction. A cell transformation was carried out and a cubic cell with an axial length of 10.26 - 10.28 Å was found. The structure solution was then attempted using this transformation on the indices and found to solve with the potassium hexachloroplatinate(IV) structure $K_2[PtCl_6]$ in the cubic crystal system with the space group Fm3m. The reflections used to find the initial unit cell were then entered into an array on the computer and the unit cells recalculated, and a transformation using the diffractometer software also produced the cubic unit cell. The crystal data and data collection parameters for the cubic cell are given in Tables 10.8 and 10.9. Merging of equivalent reflections resulted in 111 unique reflections with an intensity greater than 3σ which were used in the structure solution and refinement.

Formula	$(H_3O)_2[IrBr_6]$
Formula weight	709.67
Crystal system	Cubic
Space group	Fm3m
a	10.2738(28) Å
$\alpha = \beta = \gamma$	90.000(0)°
Volume	1084.39(89) $Å^3$
F(000)	1211
μ	341.28 cm^{-1}

TABLE 10.8

Crystal data for $(H_3O)_2[IrBr_6]$

Temperature	123 K
Radiation	Mo K_α (0.71069a)
Scan range	2.2^o
Scan speed	fixed 4.88 ^{o} min^{-1}.
Crystal dimensions	0.1mm x 0.14mm x 0.16mm
Crystal volume	0.0015 mm^3
Calculated density	4.35 g cm^{-3}
Measured density	> 3.31 g cm^{-3}
Molecules per unit cell	four
Mosaicity	$< 0.3^o$
Reflections used in refinement	111
Ratio observations to variables	111:6 (18.5:1)
Range of transmission factors	0.521 - 0.958

TABLE 10.9

Data collection parameters for $(H_3O)_2[IrBr_6]$

The atom positions were taken from another structure [Rankin 1978] and after four cycles of refinement R dropped to 0.08. Weighted least squares refinement with anisotropic thermal parameters for all atoms led to a final R of 0.0317, a R_w of 0.0237, and a goodness of fit of 1.341. The atom positions and thermal parameters are given in Tables 10.10 and 10.11. No attempt was made to locate the hydrogen atoms and it is evident from the site symmetry of the oxygen atom ($\bar{4}3m$) that they must be disordered.

The final electron density difference map showed no anomalies and the peaks in the difference Fourier are concentrated around the heavy atoms and are most likely to be associated with residual anisotropy.

10.3.4 Description of the Structure

The origin in the space group Fm3m has site symmetry m3m and this means that there is only one unique bond, the rest being generated by the symmetry requirements of the space group. Thus the coordination of the anionic unit is crystallographically required to be perfectly octahedral.

10.3.5 Discussion

The bond length of 2.515(1) Å is similar to that found in the tetragonal unit cell of 2.510(1) and 2.509(1) Å. It is interesting that when the structure was solved in the lower symmetry tetragonal space group the two "independent" bond lengths were the same within the standard deviation. This occurred even when there was no crystallographic requirement for them to be the same. This suggested

Atom	x	y	z	U*
Ir	0	0	0	20(1)
Br	2448(1)	0	0	28(1)
O	2500	2500	2500	16(2)

TABLE 10.10

Atom coordinates ($\times 10^4$) and temperature factors ($\times 10^3$) for $(H_3O)_2[IrBr_6]$.

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir	20(1)	20(1)	20(1)	0	0	0
Br	16(1)	33(1)	33(1)	0	0	0
O	15(2)	15(2)	15(2)	0	0	0

TABLE 10.11

Anisotropic temperature factors ($\mathring{A}^2 \times 10^3$) for $(H_3O)_2[IrBr_6]$

that the lower symmetry cell was incorrect and may serve as an indicator of higher symmetry.

There is little data available on Ir-Br bond lengths and those reported are for Ir(III)-Br bonds. Surprisingly the Ir(III)-Br bond lengths reported are similar to the bond length obtained here for Ir(IV)-Br. Rankin et al. (1983) reported Ir-Br bond lengths in the range 2.486(5) to 2.510(4) Å for $Rb_3[IrBr_6].H_2O$. Bottomley (1975) found Ir-Br bond lengths of 2.475(3) and 2.285(3) Å for bromine atoms opposite other bromine atoms and 2.419(4) Å for the bromine opposite the nitrosyl group in the complex $K[Ir(NO)Br_5].H_2O$. He attributed the shortening of the Ir-Br bond length to the greater π-acceptor ability of the nitrosyl group but the lesser σ-donating ability relative to the bromine atom. There is more evidence for this effect in iridium chlorine complexes where more data is available, and a similar effect was seen in the structure of $Ru(NO)Br_3(Et_2PPh)_2$ (see Chapter 7) The comparison of the limited data on bond lengths suggests there is little difference between the Ir-Br bond length for Ir(III) and Ir(IV).

It is possible that the Ir-Br bond has some Ir → Br π character, and this would be more likely for Ir(III) compared with Ir(IV). Nikol'skii et al. (1974) have investigated the relative strengths of the M-Cl σ and π bonds in $[M(NO)Cl_5]^{2-}$ on the basis of their electronic structures which were calculated by the LCAO-MO method using the CNDO approximation. The results of these calculations indicated that there is a significant π component in the M-Cl bond, which is important in stabilising the bond.

Therefore the possibility of greater π character in the Ir(III)-Br bond may be the reason why the Ir(IV)-Br bond is similar in length to the Ir(III)-Br bond.

Oxonium salts are relatively common [Shishkin & Krogius 1956; Shishkin et al. 1958] but there are few reported oxonium salts with the $A_2[MX_6]$ stoichiometry; $(H_3O)_2[OsI_6]$ [Fergusson et al. 1962], $(H_3O)_2[PtCl_6]$ [Gillard & Wilkinson 1964], $(H_3O)_2[InF_6]$ [Deichman & Britsyna 1964] and $H_2[IrCl_6].2H_2O$ [Pietsch 1939]. The oxonium salts $(H_3O)_2[IrCl_6].2H_2O$ and $(H_3O)_2[OsCl_6].4H_2O$ are available commercially [Aldrich]. In most cases the oxonium salts were found to be isomorphous with the ammonium analogue.

10.4 THE CRYSTAL AND MOLECULAR STRUCTURE OF AMMONIUM HEXABROMOIRIDATE(IV) $(NH_4)_2[IrBr_6]$

10.4.1 Introduction

The structure was solved in the cubic crystal system with space group Fm3m and the potassium hexachloroplatinate(IV) $K_2[PtCl_6]$ structure.

10.4.2 Data Collection

A dark octahedral shaped crystal was placed on the diffractometer and centred manually. Rotation photographs were used to find sufficient reflections to determine the unit cell. Refined cell parameters and standard deviations were obtained from the least squares refinement of 25 accurately centred reflections. The mosaicity of several reflections was checked in different directions through the crystal and the data collection was carried out using the ω-scan technique. Crystal stability was monitored by recording three standard reflections every 100 reflections and there was no significant variation observed. The intensities of 874 reflections were measured in the positive octant of reciprocal space and no index restrictions were applied other than this. Merging of equivalent data produced 151 unique reflections with an intensity greater than 3σ which were used in the structure solution and refinement.

The crystal and experimental parameters are summarised in Tables 10.12 and 10.13.

Formula	$(NH_4)_2[IrBr_6]$
Formula weight	707.70
Crystal system	cubic
Space group	Fm3m
a	10.440(2) Å
$\alpha = \beta = \gamma$	90.000(0)°
Volume	1137.99(54) $Å^3$
F(000)	1204
μ	325.15 cm^{-1}

TABLE 10.12

Crystal data for $(NH_4)_2[IrBr_6]$

Temperature	123 K
Radiation	Mo K_α (0.71069a)
Scan range	2.4^o
Scan speed	fixed 4.88 $^o min^{-1}$.
Crystal dimensions	0.26mm x 0.24mm x 0.16mm
Crystal volume	0.010 mm^3
Calculated density	4.13 g cm^{-3}
Measured density	> 3.31 g cm^{-3}
Molecules per unit cell	four
Mosaicity	0.28^o
Observed reflections	874
Reflections used in refinement	151
Ratio observations to variables	151:6 (25:1)
Range of transmission factors	0.015 - 0.057

TABLE 10.13

Data collection parameters for $(NH_4)_2[IrBr_6]$

10.4.3 Structure Solution and Refinement

The data was treated for Lorentz and polarisation effects and the atom positions from an analogous structure entered and allowed to refine.

An empirical absorption correction was found to produce a slightly better result than a Gaussian face indexing procedure. This correction used equivalent reflections from the original data set which were sorted and used to calculate the absorption. For the correction applied here, the merging R value before the correction was 0.0963, and after was 0.0647. The maximum transmission factor was 0.057 and the minimum was 0.015.

All atoms were assigned anisotropic thermal parameters and a weighted least squares procedure allowing the weighting parameter to vary was used at the end of the refinement. This led to a final R of 0.0916, a weighted R of 0.0889, and a goodness of fit of 4.837.

Comparison of the observed and and calculated structure factors showed no evidence of extinction and no attempt was made to locate the hydrogen atoms. The final electron density difference map showed no serious anomalies and the residual peaks are concentrated around the heavy atoms and are most likely to be associated with residual anisotropy.

10.4.4 Description of the Structure

The structure is the same as reported for the potassium hexachloroplatinate complex $K_2[PtCl_6]$ [Wycoff 1965] with the iridium atom on a special position of site symmetry m3m and the cation on a position of symmetry $\bar{4}3m$. There is only one unique Ir-Br bond length and this was found to be 2.549(3) Å.

The atom coordinates and the anisotropic temperature factors are given in Tables 10.14 and 10.15.

10.4.5 Discussion

The relatively high R of 0.091 indicates that this structure is not fully refined. Attempts were made to solve the structure in the lower Laue symmetry equivalent space group Fm3 and the tetragonal space group I4/mm. Neither of these produced any improvement and the higher symmetry cubic space group seems to be the correct one. The absorption correction did not produce the spectacular improvement for R that has been noted with other complexes of this type and this may be due to the relatively even shape of the crystal, or the inadvisability of applying an empirical correction that was based on equivalent reflections and not on an independant data set obtained from ψ-scans. However there is no obvious reason why the Gaussian face indexing procedure did not produce a significant improvement and the overall lack of refinement may ultimately reflect the crystal quality. The peak profiles were observed to be symmetrical, but they were also quite broad and a relatively wide scan range (2.4^{o}) was necessary in the data collection.

As discussed above there is little data available on Ir-Br bond lengths. The only Ir-Br bond length reported for Ir(IV) is that for the complex $(H_3O)_2[IrBr_6]$ described in Section 10.3. The Ir-Br bond length for the ammonium complex is similar to that of the oxonium complex 2.515(1) Å and also for those in Ir(III) bromo- complexes which are in the range 2.486(5) - 2.510(4) Å.

Atom	x	y	z	U *
Ir	0	0	0	110(1)
Br	2442(3)	0	0	21(1)
N	2500	2500	2500	16(2)

TABLE 10.14

Atom coordinates (x 10^4) and temperature factors (x 10^3) for $(NH_4)_2[IrBr_6]$

* (Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir	110(1)	110(1)	110(1)	0	0	0
Br	7(1)	29(1)	29(1)	0	0	0
N	27(1)	27(1)	27(1)	0	0	0

TABLE 10.15

Anisotropic temperature factors ($Å^2$ x 10^3) for $(NH_4)_2[IrBr_6]$

10.5 THE CRYSTAL AND MOLECULAR STRUCTURE OF POTASSIUM PENTACHLORO(TRICHLOROSTANNATO)IRIDATE(III) $K_3[IrCl_5(SnCl_3)]$

10.5.1 Introduction

The preparation of the complex $K_3[IrCl_5(SnCl_3)]$ was achieved using the method reported for the rhodium complex $Cs_3[RhCl_4(SnCl_3)_2]$ (see Chapter 9). The intention was to produce a bis-trichlorotstannato- analogue for iridium, but the X-ray analysis found that there was only one trichlorostannato- ligand attached to the iridium atom. The structure was solved in the orthorhombic crystal system with the space group $Pmn2_1$.

10.5.2 Data Collection

A dichroic red-green thin plate crystal was placed on the diffractometer and centred manually. Refined cell parameters and standard deviations were obtained from the least squares refinement of 25 accurately centred reflections. The mosaicity of several reflections was checked in different directions through the crystal and the data collection was carried out using the ω-scan technique. Crystal stability was monitored by recording three standard reflections every 100 reflections and no significant variation was observed. The intensities of 1031 reflections were measured in the positive octant of reciprocal space. Of these 863 reflections had an intensity greater than 3σ and were used in the structure solution and refinement.

The crystal and experimental parameters are summarised in Tables 10.16 and 10.17.

10.5.3 Structure Solution and Refinement

The systematic absences were consistent with two space groups, Pmmn, and $Pmn2_1$. Attempts to solve the structure in the space group Pmmn were unsuccessful, and the structure was eventually solved in the space group $Pmn2_1$.

The data was treated for Lorentz and polarisation effects and the position of the iridium atom deduced from the Patterson map. The difference map showed that there were two atoms attached to the iridium with bond lengths of ca. 2.50 Å. It was thought that these atoms were both tin but the struture would not refine (R ca. 0.30) when tin atoms were used in the model. However, when one of the atoms was replaced with a chlorine atom the fit improved to an R of 0.1699. The remaining atoms were located from difference maps and the refinement convirged to a R of 0.1088.

An empirical absorption correction using a thin plate model led to a dramtic improvment in the refinement of the structure. The range of transmission factors was 0.201 - 0.776 and this indicates the importance of the absorption correction for this crystal. Application of this correction gave an R of 0.0475.

All atoms were assigned anisotropic thermal parameters and a weighted least squares procedure, allowing the weighting to vary, was used at the final stages of the refinement. This led to a final R of 0.0251, a weighted R of 0.0254, and a goodness of fit of 0.852.

Formula	$K_3[IrCl_5(SnCl_3)]$
Formula weight	711.82
Crystal system	orthorhombic
Space group	$Pmn2_1$
a	9.5873(13) Å
b	9.5170(15) Å
c	7.8480(9) Å
$\alpha = \beta = \gamma$	90.000(0)°
volume	716.11(17) $Å^3$
F(000)	640
μ	133.45 cm^{-1}

TABLE 10.16

Crystal data $K_3[IrCl_5(SnCl_3)]$

Temperature	163 K
Radiation	Mo K_α (0.71069a)
Scan range	2.0°
Scan speed	fixed 4.88 $^\circ min^{-1}$.
Bragg angle range	$5 - 55^\circ$
Crystal dimensions	0.40mm x 0.24mm x 0.02mm
Crystal volume	0.002 mm^3
Calculated density	3.30 g cm^{-3}
Measured density	> 3.31 g cm^{-3}
Molecules per unit cell	two
Mosaicity	0.28°
Observed reflections	1301
Reflections used in refinement	863
Ratio observations to variables	863:69 (12.5:1)
Range of transmission factors	0.201 - 0.776

TABLE 10.17

Data collection parameters for $K_3[IrCl_5(SnCl_5)]$

Comparison of the observed and and calculated structure factors showed no evidence of extinction. The final electron density difference map showed no anomalies and the residual peaks are concentrated around the heavy atoms and are most likely to be associated with residual anisotropy.

The space group $Pmn2_1$ is a polar space group and the origin lies on the intersection of the mirror plane and the glide plane, and may have any value for the z coordinate. Hence it was necessary to define the origin by fixing the z coordinate of one of the atoms. The z coordinate of the heaviest atom, the iridium atom, was fixed to define the origin.

10.5.4 Description of the Structure

The five chlorines atoms and the $SnCl_3^-$ ligand are attached to the iridium atom in an octahedral manner. The coordination around the iridium is close to an ideal octahedron with only small deviations in theoretical bond angles. The molecule has m symmetry with the Ir, the Sn and four of the chlorines on the mirror plane.

The structure of the anionic unit is given in Figure 10.3, and the unit cell packing in Figure 10.4. The atom coordinates and the anisotropic temperature factors are given in Tables 10.18 and 10.19.

The low R of 0.0251 and small standard deviations in the atomic coordinates and bond lengths shows that the structure is well refined.

10.5.5 Discussion

Although many platinum metal complexes containing trichlorstannato- ligands are known, there have been few X-ray

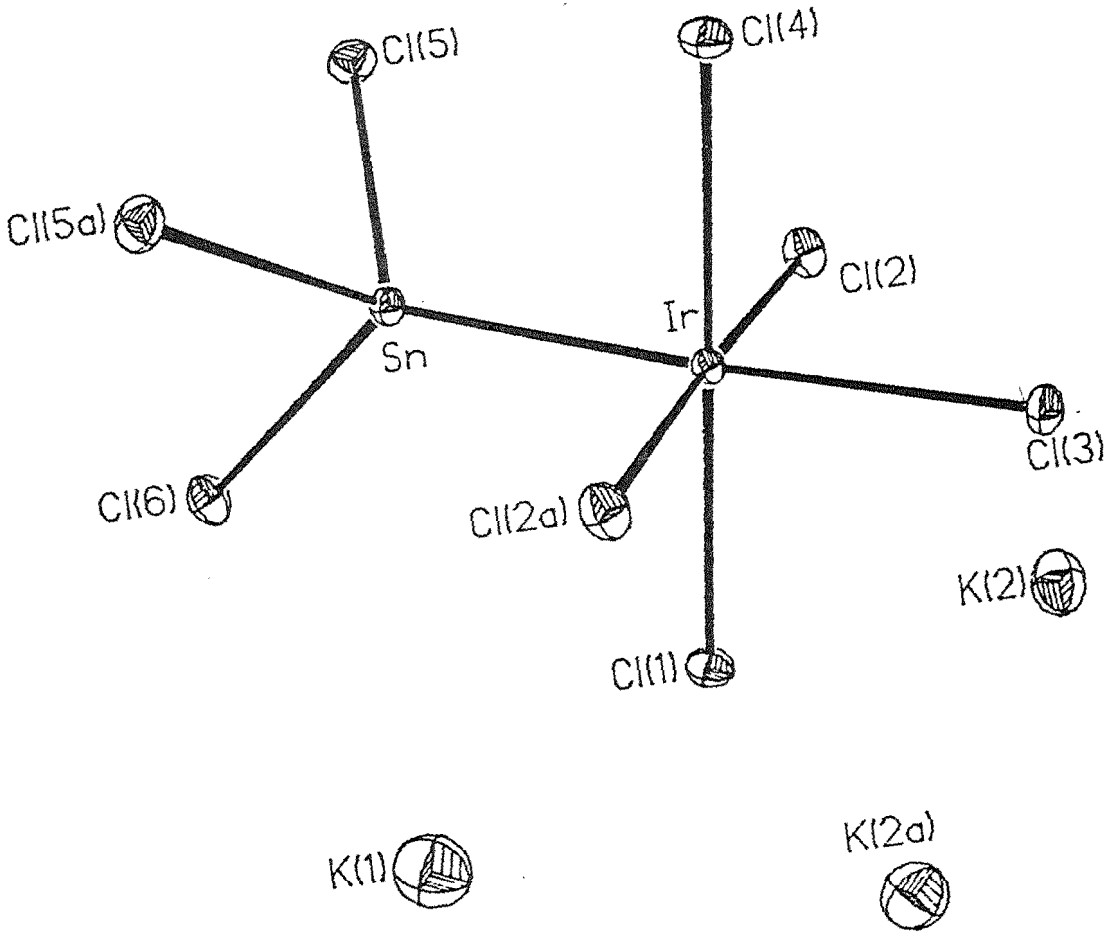


FIGURE 10.3

Perspective view of the structure of $K_3[IrCl_5(SnCl_3)]$

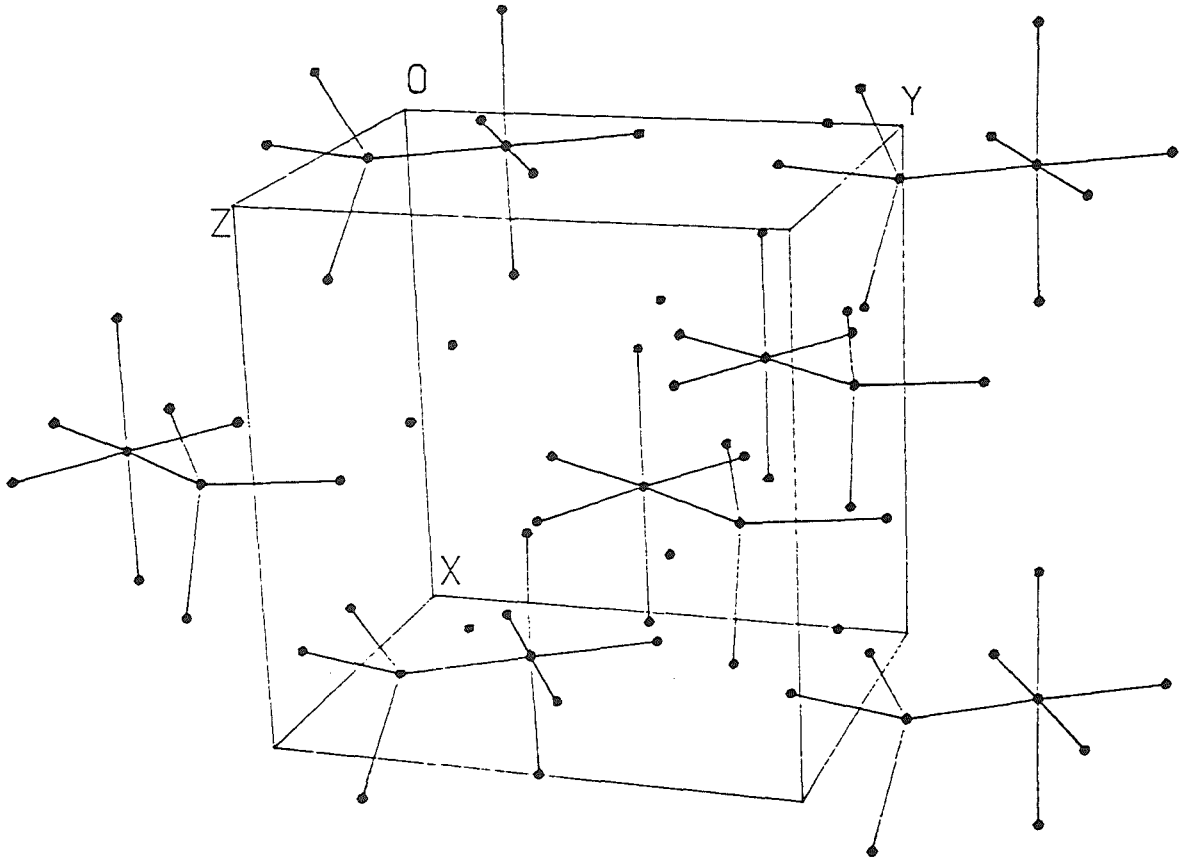


FIGURE 10.4

Unit cell packing for $K_3[IrCl_5(SnCl_3)]$

Atom	x	y	z	U *
Ir	0	3102(1)	-6582(0)	11.4(1)
Sn	5000(0)	9060(1)	-9781(1)	12.4(2)
C1(1)	5000(0)	8148(3)	-4148(4)	18.9(10)
Cl(2)	7522(2)	3122(2)	-6637(5)	20.2(6)
Cl(3)	0	5292(4)	-8196(5)	18.3(9)
Cl(4)	0	4367(4)	-3981(5)	20.9(9)
Cl(5)	8114(2)	661(3)	-2848(3)	22.3(6)
Cl(6)	0	-1431(4)	-5695(5)	22.3(10)
K(1)	0	-1407(7)	24(9)	60.5(19)
K(2)	7587(3)	3733(3)	- 679(4)	36.0(9)

TABLE 10.18

Atom coordinates (x 10^4) and temperature factors (x 10^3) for $K_3[IrCl_5(SnCl_5)]$.

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir	12.3(2)	9.4(2)	11.9(2)	0(2)	0(0)	0(0)
Sn	13.5(4)	11.0(4)	12.8(4)	0(3)	0(0)	0(0)
Cl(1)	25.2(17)	17.6(18)	13.9(15)	6.3(12)	0(0)	0(0)
Cl(2)	15.4(9)	18.9(11)	26.2(11)	1.0(10)	-1.8(15)	0(1)
Cl(3)	23.2(15)	12.8(15)	18.9(16)	4.4(13)	0(0)	0(0)
Cl(4)	26.9(16)	19.7(18)	15.9(14)	-0.5(1)	0(0)	0(0)
Cl(5)	20.1(10)	26.1(12)	20.8(10)	1.8(9)	4.5(10)	-0.1(1)
Cl(6)	25.2(18)	13.2(16)	28.3(20)	-0.6(15)	0(0)	0(0)
K(1)	56.2(28)	64.6(36)	60.8(35)	-6.6(30)	0(0)	0(0)
K(2)	37.3(14)	33.4(16)	37.2(16)	1.8(11)	-6.0(10)	2.0(12)

TABLE 10.19

Anisotropic temperature factors ($Å^2 \times 10^3$) for $K_3[IrCl_5(SnCl_5)]$

structural determinations reported. There have been single crystal X-ray structure determinations reported for iridium [Porta et al. 1967; Churchill & Lin 1974], but these complexes were organometallic in nature and only contained one trichlorostannato- ligand. The X-ray structures of halogeno- complexes containing trichlorostannato- ligands have been reported for osmium and rhodium [Farrugia et al. 1982; Faruggia et al. 1981; Khodashova et al. 1980; Czeska et al. 1983].

The Ir-Sn bond length found in the present work of 2.496(1) Å is short compared with that reported for other complexes, 2.642(2) Å [Porta et al. 1967], and 2.587() Å [Churchill & Lin 1974]. Farrugia et al (1981) in the complex $(TEA)_4[RuCl(SnCl_3)_5]$ found that the Ru-Sn bond length was shorter for the $SnCl_3^-$ ligand that was bound opposite Cl compared with that opposite another $SnCl_3^-$ ligand. A similar effect was seen for the complex $(NH_4)_4[OsCl(SnCl_3)_5]$ [Khodashova et al. 1980].

There is a considerable spread in the range of Sn-Cl bond lengths reported; 2.340(4) - 2.42(2) Å and the Sn-Cl bond lengths of 2.369(4), and 2.375(3) Å found in the present work lie within this range. Most of the reported Sn-Cl bond lengths lie at the top of the range and the values found here are relatively short compared with the reported values [Porta et al. 1967; Czeska et al. 1983; Consiglio et al. 1983; Churchill & Lin 1974; Farrugia et al. 1982; Farrugia et al. 1981; Khodashova et al. 1980].

A further feature of the structure is the variation of the Ir-Cl bond length. The Ir-Cl bond length for the chlorine opposite the Sn is significantly longer at 2.438(3) Å, compared with the others which are in the range 2.339(3) - 2.376(2) Å. These values compare with the

values of 2.352(5) - 2.373(4) Å in the complex $K_3[IrCl_6]$ (Section 10.2) and the long Ir-Cl bond length found for the trans chlorine is also longer than those found in other Ir(III) complexes [Rankin et al. 1983]. The M-Cl bond length for other reported structures also showed lengthening of the M-Cl bond for the chlorine opposite the $SnCl_3^-$ ligand [Farrugia et al. 1982; Farrugia et al. 1981; Khodashova et al. 1980]. The lengthening of the M-Cl bond for the Cl opposite the $SnCl_3^-$ group for all three metals is in contrast to the effect seen in nitrosyl complexes. Nitric oxide is regarded as being a weak σ-donor and a good π-acceptor and the difference in behaviour between NO^+ and $SnCl_3^-$ suggests that σ-bonding may be important in stabilising the M-Sn bond. It is interesting that in the complex $(PPh_4)_2[OsCl_3(NO)(SnCl_3)_2]$ that the $SnCl_3^-$ ligands were found in the trans configuration [Czeska et al. 1983]. The fact that the $SnCl_3^-$ ligand does not bind opposite the good σ-donor chlorine, or the good π-donor NO^+, suggests that the formation of a π-bond also contributes to the stabilty of the M-Sn bond.

It is interesting that the mono-trichlorostannato- complex was formed when under the same reaction conditions the bis-trichlorstannato- rhodium complex was obtained. It appears that the $SnCl_3^-$ ligand is quite labile in Ir(III) complexes, and as described in Chapter 9 it proved difficult to isolate trichlorostannato- complexes of iridium. In view of the X-ray structure this is somewhat surprising, considering the apparent strong Ir-Sn bond. The lengthening of the Ir-Cl bond length suggests that the $SnCl_3^-$ ligand exerts a considerable trans effect and this may explain why no trans bis-trichlorostannato- complex was isolated. The cis complex may not be formed due the the apparent reluctance of the

$SnCl_3^-$ ligand to bind opposite strong σ-donors such as chlorine, and it is possible that this effect is greater for Ir(III) than other platinum metals. The bond lengths are given in Table 10.20 and the bond angles in Table 10.21.

Bond	Length	Bond	Length
Ir - Sn	2.496(1)	Ir - Cl(1)	2.339(3)
Ir - Cl(2)	2.376(2)	Ir - Cl(3)	2.438((3)
Ir - Cl(4)	2.370(4)	Sn - Cl(5)	2.375(3)
Sn - Cl(6)	2.369(4)		

TABLE 10.20

Bond lengths (Å) for $K_3[IrCl_5(SnCl_5)]$

Bond	Angle	Bond	Angle
Cl(1) - Ir - Cl(4)	180.0(0)	Cl(1) - Ir - Cl(2)	89.3(1)
Cl(1) - Ir - Cl(3)	89.3(1)	Cl(3) - Ir - Sn	176.8(1)
Cl(1) - Ir - Sn	93.9(1)	Cl(5) - Sn - Ir	117.0(1)
Cl(6) - Sn - Ir	127.9(1)	Cl(5) - Sn - Cl(6)	95.0(1)

TABLE 10.21

Selected bond angles (deg) for $K_3[IrCl_5(SnCl_3)]$

10.6 THE CRYSTAL AND MOLECULAR STRUCTURE OF AMMONIUM PENTACHLORO(TRICHLOROSTANNATO)IRIDATE(III) $(NH_4)_3[IrCl_5(SnCl_3)]$

The complex $(NH_4)_3[IrCl_5(SnCl_3)]$ was found to be isomorphous with the K^+ salt described in Section 10.5. Refined unit cell parameters were determined from a single crystal on the X-ray diffractometer; a = 9.593(3), b = 9.495(2), c = 7.832(2) Å, and V = 713.34(30) $Å^3$. Precession photography showed that the systematic absences were the same as for the K^+ salt.

CHAPTER 11

PHYSICAL METHODS EMPLOYED IN THIS THESIS

11.1 INFRARED SPECTROSCOPY

Infrared spectra were measured between 200 and 4000 cm^{-1} using either a Shimadzu IR-27G spectrophotometer or a Pye Unicam SP3-300 spectrophotometer. The solid samples were measured as pressed potassium bromide disks and the solution infrared spectra in a potassium bromide cell using chloroform as the solvent. All spectra were referenced using polystyrene reference peaks.

11.2 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

The ^{1}H spectra were recorded at 60 MHz using a Varian T60 spectrometer and for the less soluble complexes or, when more detail was required, using a Varian XL 300 spectrometer which operated at 299.93 MHz. All ^{13}C spectra were measured using the Varian XL 300 spectrometer. Deuterated chloroform was the usual solvent employed but d_6-dimethylsulphoxide was used when the compound was especially low in solubility.

11.3 ELECTRONIC ABSORPTION SPECTROSCOPY

The spectra were measured on a Varian DMS-100 spectrometer between 200 and 800 nm using 1 cm quartz cells. The molar absorptivity ε was calculated from the expression;

$$A = \varepsilon c l$$

where c = the concentration in moles litres $^{-1}$

and l = the cell pathlength in cm.

11.4 X-RAY SINGLE CRYSTAL ANALYSIS

11.4.1 Introduction

All the programs used for data reduction and structure solution are contained in the SHELXTL (version 4) package [Sheldrick 1984].

11.4.2 Preliminary Studies

All the compounds studied in this thesis were investigated prior to the data collection by precession photography using the Buerger method and Mo K_α radiation. The crystal was mounted on a glass fibre with a crystal face perpendicular to the incident X-ray beam. The crystal orientation was completed from corrections deduced from the setting photographs. These studies gave an indication of the crystal quality and enabled the determination of unit cell parameters. In most cases probable space group were also obtained.

11.4.3 Instrument Description

The data collections were carried out on a Nicolet R3m four circle X-ray diffractometer using Mo K_α radiation. All but one of the data collections were carried out at low temperature by bathing the crystal in a stream of cold nitrogen gas. The temperature obtained was in the range 120 - 170 K. The crystals were mounted on a glass

fibre in a random orientation using oil or vaseline. For the room temperature data collection the crystal was glued to the fibre using a rapid setting epoxy resin.

11.4.4 Data Collection Methods

A total of twenty-five accurately centred reflections were used to calculate unit cell parameters and their standard deviations. Because of the lack of constraints the intial unit cell obtained was often a triclinic cell. The diffractometer software has a cell transformation program that is used to check for the higher symmetry. In many instances the program failed to find the correct cell and it was only after the data collection when the structure solution proved impossible that the correctness of the cell was suspected. Cell transformations using another independent program were a little more successful, but still several times failed to produce the correct cell. Even if the incorrect cell is obtained, systematic absences consistent with known space groups are still evident and so this does not serve as a guide to the correctness of the space group assignment.

The mosaicity of several strong low angle reflections was checked before beginning the data collection. The mosaicity of the crystal is evaluated by inspection of the peak profiles and these should be symmetrical in nature and relatively narrow. The width at half-height is used as a measure of the crystal quality and should be in the region of $0.2 - 0.4^{\circ}$. For the crystals examined in this thesis the width at half-height was usually 0.30° or better.

The intensity of the reflections was measured using the ω-scan technique and in one case Wycoff-ω scans. In the ω-scan technique the

counter is held stationary and the crystal is rotated in the-ω circle. The Wycoff-ω is similar to the ω-scan technique except that whereas for the ω-scan technique the reflection profile is measured by sampling at 96 points, in the Wycoff-ω scans only five points are measured. This is a much more rapid method and is used when there is some danger of crystal deterioation or when a rapid data collection is required. The other technique commonly used is the θ-2θ technique. In this method the counter moves as well as the crystal but at a rate twice that of the crystal. Previous work in this department found that best results are produced when the ω-scan technique was used.

11.4.5 Data Reduction

The raw data was treated in a data reduction step. This involved allowing for the effects of polarisation, the Lorentz factor and profile fitting of the reflections.

a) Polarisation effects

The X-ray beams were passed through a graphite monochromator. This involves reflection from a crystal surface and leads to the monochromated beam being slightly polarised. Each electric vector of the unpolarised beam has two components which are initially of equal strength. When the beam is reflected from a crystal surface, the waves having their electric vector parallel to reflecting plane are reflected to an extent which is dependant only on the electron density of the plane. The other vector also has an angular dependance and this means that there is a difference in the strength of the electric vectors after reflection and thus a partial polarisation occurs.

b) Lorentz correction

Lorentz corrections are required since in most single crystal methods the specimen is given a controlled movement through the X-ray beam. Various planes are thereby presented to the beam at their respective Bragg angles and given the opportunity to reflect. The rate at which the planes pass through the Bragg condition varies with the diffraction angle and thus each intensity measurement must be corrected for the difference in time taken to be measured.

c) Profile Fitting

A profile fitting procedure was applied in which the reflection profile is smoothed to fit a symmetrical shape with even backgrounds. This improves the precision of weak reflections which is sometimes important because of uneven backgrounds.

11.4.6 Structure Solution Methods

a) The Patterson Function

The Patterson map was used to find the heavy transition metal atom. This was usually quite straight forward because of the large size of the atom relative to the other atoms in the structure. This is a common method of obtaining at least partial structures. Patterson showed that whereas a Fourier calculation using structure factors gave the atom positions in the unit cell, a similar Fourier calculation using $|F|^2$ gives peaks corresponding to all the interatomic vectors. From this vector list the atomic positions can be deduced. The main

problem with the Patterson map is that if there are many atoms in the unit cell then there are many vectors generated and the map becomes too complex to unravel. Once the transition metal atom was located it was possible to solve the structure via the heavy atom method.

b) The Heavy atom method

The general expression for the structure factor is

$$F_{hkl} = \sum f_j \exp[2\pi i(hx_j + ky_j + lz_j)]$$

When a heavy atom is present, because it has a very large X-ray scattering factor f_j it dominates this summation. An estimate of the phase based only on the heavy atom is usually sufficiently accurate to produce a trial electron density map. A measure as to the likely success of the heavy atom method is given by the Sim quotient;

$$Z^2(\text{heavy}) \; / \; \sum Z^2(\text{light})$$

If the value of the Sim quotient is greater than one, then a reasonably reliable trial map can be obtained from which the positions of any other heavy atoms may be deduced. When these atoms are used in the model of the structure, the estimate of the phase is much more reliable, and thus a much better trial map is obtained from which the lighter atoms are found readily. Structures such as the ones investigated in this work are ideal for heavy atom methods due to the domination of the structure factor summation by the large transition metal atoms. A furthur consequence of this is that lighter atoms

cannot be located precisely in the presence of heavier atoms because the light atoms contribution to the structure factor summation is small.

11.4.7 Absorption Corrections

There are two different methods that can be used to correct for absorption effects. Each method has different advantages and in several cases both were attempted and that which produced the better result was used.

a) Empirical methods

Absorption correction by an empirical method involves selecting several reflections and measuring their intensities in different directions through the crystal by adjusting χ and ψ. Six parameters are used to define a psuedo-ellipsoid which is used to calculate the correction required. A merging R factor which is a measure of the agreement of the intensities is produced before and after the application of the correction, and the best model is that which leads to the best agreement of the measured intensities. This model is then used to treat the whole data collection. In addition to the ellipsiodal model, a thin plate model may be used. This requires the indices of the principal face and three parameters are used to define the crystal as a thin plate.

b) Gaussian Face Indexing

In this method the faces of the crystal are indexed and the dimensions are measured precisely. The linear absorption coefficient and crystal dimensions are used to calculate the reduction in intensity of the diffracted beam for the different path lengths through the crystal. This is the best method to use when the crystal faces are clearly defined and can lead to dramatic improvements in the structure refinement. It is not practical to use this method when the crystal is very thin or there are a large number of faces. The method is very sensitive to the dimensions of the crystal and it is important for the success of this method that they can be measured reliably.

11.4.8 Extinction Corrections

There are two types of extinction; primary and secondary. Primary extinction occurs in near perfect crystals because the reflected X-ray beams are re-reflected by the undersides of the reflecting faces. This is seen as a systematic lowering of the observed structure factor relative to the calculated value for all reflections. Most crystals do not contain extended regions of perfect planes but are composed of small mosaic blocks. In a crystal with some mosaicity re-reflections are less likely and primary extinction is rarely encountered.

Secondary extinction arises for reflections that appreciable amounts of the incident beams are reflected by the first planes that are encountered by them and thus the deeper planes recieve less incident intensity. This means that the whole crystal is not exposed to the full incident radiation, and a thus lowering of the reflected

intensity results. This is most evident for low angle reflections and shows up as a systematic lowering of the intensity of the more intense reflections. Evidence for secondary extinction was seen during the refinement of the structure for $K_3[IrCl_6]$ and was allowed for using the formula;

$$F_c(\text{corr.}) = F_c / [(1.0 + 0.002\ (x)\ F^2/\sin(2\theta)]^{0.25}$$

where x is the secondary extinction coefficient.

11.4.9 Thermal Vibration

The effects of thermal vibration were allowed for by incorporating an adjustment to the scattering factor of the general form;

$$f_{(\text{thermal } j)} = f_{(\text{stationary } j)} \times t_{(j)}$$

and for the isotropic case the value of $t_{(j)}$ is given by;

$$t_{j\ iso} = \exp[-B_{iso}(\sin^2\theta)/\lambda^2]$$

where $B_{iso} = 8\pi^2u^2$ and u is the mean square amplitude of the vibration. For the anisotropic case the value of $t_{(j)}$ is given by

$$t_{j\ anis} = \exp[-2\pi^2[U_{11}h^2a^{*2} + U_{22}k^2b^{*2} \ldots\ldots + 2U_{23}klb^*c^*\cos(\alpha^*)]]$$

11.4.10 Hydrogen Atom Location

The location of hydrogen atoms in the presence of heavy atoms such as third row transitions metals is very difficult. The model is relatively insensitive to the positions of atoms with higher atomic weights than hydrogen such as carbon and oxygen. The SHELXTL system allows for the generation of calculated hydrogen atom positions and this was done in the structure of $Ru(NO)Br_3(Et_2PPh)_2$. The type of hydrogen atom desired (primary, secondary, or tertiary) is fixed to the carbon atom and the isotropic thermal parameters are estimated from that carbon. This is an effective method of allowing for hydrogen atoms without increasing the number of variables required in the calculations significantly. Hydrogen atoms were not calculated for the other structures because the observations to variables ratio was already low. If hydrogen atoms were allowed for in these structures, this would lead to a reduction in the precision of the atomic coordinates for the other atoms.

11.4.11 Least Squares Refinement

The refinement of the trial structures was carried out using a blocked-cascade least squares procedure including anomalous dispersion corrections (see Section 11.4.12). The function minimised was;

$$\sum w(|F_o|^2 - |F_c|^2)$$

where $w = [\sigma^2(F_o) + gF_o^2]^{-1}$

A fixed value was used for the weighting parameter g at the early stages of the refinement, and at the final stages this was allowed to vary.

11.4.12 Absolute Molecular Configuration

In a first order analysis of X-ray diffraction using only real atomic scattering factors, it is not possible to distinguish between a reflection and its Friedel equivalent. In this study use was made of the effect of anomalous scattering. If the frequency of the radiation used is near the natural absorption frequency of an atom this introduces an anomalous phase change during scattering by the electrons associated with the absorption edge. The effect of anomalous scattering is allowed for by using a complex form of the scattering factor;

$$f_o(\text{anom}) = f_o + \Delta F' + i\Delta F''$$

where f_o = normal scattering factor

$\Delta F'$ = real correction term

$\Delta F''$ = imaginary component

The anomalous scattering effect introduces a phase change between Friedel equivalents and it is possible to distinguish between them. In practice the structure is inverted and the agreement between the calculated and observed structure factors compared. The enantiomorph which produces the best agreement is the correct configuration.

11.5 X-RAY POWDER DIFFRACTION

Samples were finely ground and placed on glass slides or aluminium plates. The diffractograms were measured using a Philips PW 1729 X-ray generator and a Philips PW 1710 diffractometer control unit and Cu K_α radiation. Peaks were located using a peak search routine [SHADOW] on an IBM computer and the diffractogram plotted as a pattern using a Hewlett Packard HP 7475A plotter.

11.6 X-RAY FLUORESENCE SPECTROSCOPY

This technique was used as a qualitative method of determining the presence of iridium and tin in some complexes. The spectra were measured on a Philips instrument with a Philips PW 1732/10 X-ray generator and a PW 1400/00 sample handling system. The spectra were measured using a LiF (2 0 0) diffracting crystal and a chromium tube. The sample was not powdered but a few crystals were spread out on a mylar film and their spectra measured. The advantage of this technique is that the crystalline sample remained intact and could then be used for single crystal X-ray diffraction analysis.

11.7 VACUUM LINE TECHNIQUES

The general procedures as described by Sanderson (1948) and Shriver (1969) were used. A hydrocarbon vacuum grease (Apiezon L) was used. An oil diffusion pump was necessary to obtain a good vacuum and silicone oil was used. Several days of pumping were required to remove volatile material from the oil before a good vacuum was achieved.

11.8 CALIBRATION OF THE McLEOD GAUGE

The calibration of the McLeod gauge was achieved using a MKS Baratron capacitance manometer. In a capacitance manometer the capacitor is formed from a fixed plate and a membrane. One side of the membrane is sealed under a known pressure and the other side is open to the vacuum line. When the pressure varies, this gives rise to a variation in the distance between the plates and thus in the capacitance. The manometer is calibrated when it is manufactured and can be used to obtain the pressure in the vacuum line. Figure 11.1 shows how the manometer was used to calibrate the McLeod gauge. When the McLeod gauge is in the position shown in Figure 11.1(A) the pressure in the vacuum line and the gauge is the same (P_1). When the McLeod gauge is in the position shown in Figure 11.1(B) the gas is compressed to a new pressure P_2. This pressure is equal to the height in mm of mecury shown and the volume V_2 that the gas now occupies is equal to the height (h) times the area of the tube;

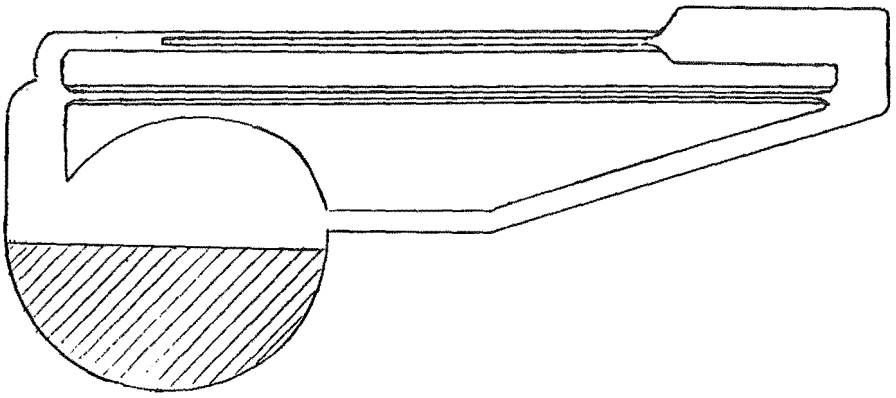
i.e. $P_1V_1 = P_2V_2$

$= h \times (\text{area} \times h)$

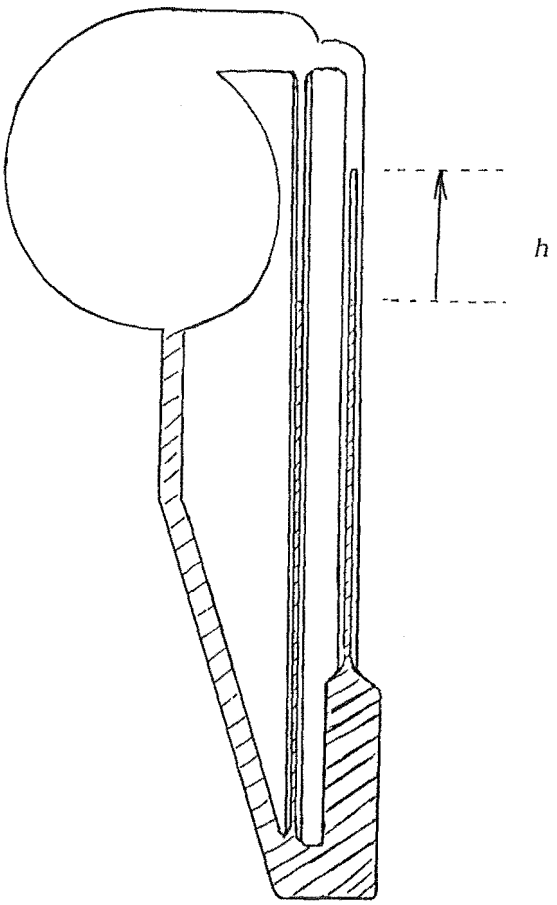
so $P_1 = h^2(\text{area} / V_1)$

Since area / V_1 will be a constant then this becomes;

$$P_1 = h^2 \times K$$



(A) $P_1 = P_2$



(B) $P_2 = h$

FIGURE 11.1

Calibration of the McLeod gague

Using the capacitance manometer the value of P_1 was measured for several different levels of vacuum (and thus several values of h) and an average value for K calculated. In principle it is possible to find K from only one measurement of P_1, but a better value is obtained by averaging several results.

Once the value of K is known the measurement of a change in the vacuum by the change in the height of the mercury in the McLeod gauge enabled the calculation of the pressure change when a gas was produced from a chemical reaction.

11.9 ELEMENTAL ANALYTICAL RESULTS

Carbon, hydrogen, nitrogen, and halide analyses were determined at the Microanalytical Laboratory, University of Otago Dunedin.

11.10 MELTING POINTS

Melting points were measured using a Kofler hot-stage apparatus.

11.11 MAGNETIC MEASUREMENTS

The magnetic susceptibility of the compounds were measured using the Guoy method. A finely powdered sample was placed in a tube and the sample placed between the poles of an electromagnet. The sample was weighed in the presence and the absence of the magnetic field and corrected for the magnetism of the glass tube.

11.12 MEASUREMENT OF pH

The pH was measured using a Beckman Research pH meter and Beckman electrodes. Two NBS buffers were employed; 0.05M potassiumhydrogenphthalate (pH = 4.008), and 0.05M potassiumtetroxalate (pH = 1.775).

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